(FILE 'HOME' ENTERED AT 16:39:12 ON 06 APR 2009)

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L2 0 S L1
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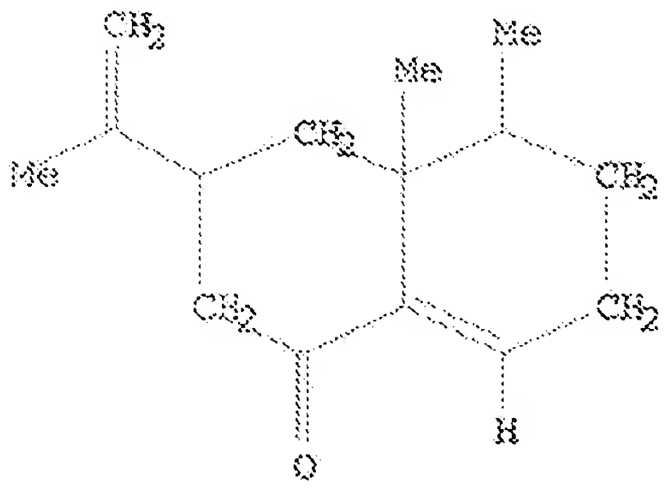

Structure attributes must be viewed using STN Express query preparation

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L4 ANSWER 1 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 2008:858562 CAPLUS
DN 150:290047
TI Volatiles from leaves and rhizomes of fragrant Acorus spp. (Acoraceae)
AU Du, Zhizhi; Clery, Robin A.; Hammond, Christopher J.
CS Kunming Institute of Botany, Kunming, Peop. Rep. China
SO Chemistry & Biodiversity (2008), 5(6), 887-895
CODEN: CBHIAM; ISSN: 1612-1872
PB Verlag Helvetica Chimica Acta
DT Journal
LA English
AB Three horticultural selections of Acorus gramineus SOLAND were investigated to determine the chemical composition of their leaves and rhizomes. The variety 'liquorice' was found to contain methylchavicol (49%) which accounts for the unusual anisic odor of this variety, while β-asarone was the main component of A. christophii (43%) and 'yodo-no-yuki' (20%). The results are compared with calamus oils, and the possible biosynthetic precursors of the main components methylchavicol and β-asarone are considered.
RE.CNT 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 2008:690058 CAPLUS
TI The botenical source of Chinese cedarwood oil: Cupressus funebris or Cupressaceae species?
AU Adams, Robert P.; Li, Shufen

CS Biology Department, Baylor University, Waco, TX, 76798, USA
SO Journal of Essential Oil Research (2008), 20(3), 235-242
CODEN: JEOREG; ISSN: 1041-2905
PB Allured Publishing Corp.
DT Journal
LA English
AB Cupressus funebris is generally regarded as the botanical source of Chinese cedarwood oil. However, due the limited amount of mature forest trees of C. funebris in China, other species in the Cupressaceae that have wood oils high in α-cedrene, β-cedrene, thujopsene and cedrol might be utilized for cedarwood oil production Wood samples of putative C. funebris were extracted and the exts. were analyzed and compared with several lots of Chinese cedarwood oil. Wood oils were also extracted from Juniperus chinensis and J. c. cv. torrulosa and analyzed. Considerable variation was found among the wood oils of putative C. funebris. The various lots of com. Chinese cedarwood oils were very variable: α-cedrene (3.6-44.2%), β-cedrene (3.5-11.5%), cis-thujopsene (1.9-37.4%), cedrol (1.7-23.4%). The presence of β-biotol and β-biotone in several Chinese cedarwood oils seems to indicate that wood of Platycladus orientalis (Biota orientalis) was utilized in their production It appears that Chinese cedarwood oil is derived from a mixture of woods from several Cupressaceae species.
RE.CNT 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 3 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 2006:822966 CAPLUS
DN 145:510879
TI Composition of the essential oil of Rhabdosciadium oligocarpum (Post ex Boiss.) Hedge et Lamond and Rhabdosciadium microcalycinum Hand.-Mazz
AU Baser, K. Husnu Can; Ozek, Gulmira; Ozek, Temel; Duran, Ahmet; Duman, Hayri
CS Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, Eskisehir, 26470, Turk.
SO Flavour and Fragrance Journal (2006), 21(4), 650-655
CODEN: FFJOED; ISSN: 0882-5734
PB John Wiley & Sons Ltd.
DT Journal
LA English
AB The volatile constituents of the oils of Rhabdosciadium oligocarpum (Post ex Boiss.) Hedge et Lamond and Rhabdosciadium microcalycinum Hand.-Mazz. (Umbelliferae) were isolated by hydrodistn. and microdistn. techniques and then analyzed by GC and GC-MS. Germacrene D was found to be the main constituent in all the oils obtained.
RE.CNT 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 4 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 2005:149534 CAPLUS
DN 143:129953
TI Essential oil composition and in vitro antimicrobial and anti-inflammatory activity of South African Vitex species
AU Nyiligira, E.; Viljoen, A. M.; Baser, K. H. C.; Ozek, T.; van Vuuren, S. F.
CS Department of Pharmacy and Pharmacology, Faculty of Health Sciences, University of Witwatersrand, Parktown, 2193, S. Afr.
SO South African Journal of Botany (2004), 70(4), 611-617
CODEN: SAJBDD; ISSN: 0254-6299
PB NISC Pty Ltd.
DT Journal
LA English
AB The essential oil composition of Vitex pooara, V, rehmannii, V. obovata ssp obovata, V. obovata ssp. wilmsii and V. zeyheri was determined using gas chromatog. and mass spectrometry. The in vitro antimicrobial activity of

the essential oils was assessed on Staphylococcus aureus, Bacillus cereus and Escherichia coli and the min. inhibitory concentration values recorded. All essential oils were moderately active with V. zeyheri being the most active (8, 4 and 16 mg ml-1 for S. aureus, B. cereus and E. coli resp.). The in vitro anti-inflammatory activity of the essential oils was evaluated using a 5-lipoxygenase assay and all essential oils effectively inhibited 5-lipoxygenase, a key enzyme in the inflammatory cascade with V. pooara producing the most promising activity (IC50 value of 25 ppm). Using the essential oil data matrix, chemotaxonomic evidence is presented which supports the infrageneric placement of V. pooara in subgenus Vitex while the other four above mentioned taxa are placed in subgenus Holmskiodiopsis.

RE CNT 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 2004:220117 CAPLUS
DN 140:248749
TI Isolation of insecticidal eremophilone and derivatives from Myoporaceae
IN Leach, David Norman; Spooner-Hart, Robert Neil; Eaton, Greg Francis
PA Bioprospect Limited, Australia
SO PCT Int. Appl., 81 pp.
CODEN: PIXXD2
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2004021784	A1	20040318	WO 2003-AU1133	20030903
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	RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
	AU 2003257249	A1	20040329	AU 2003-257249	20030903
	AU 2003257249	B2	20080626		
	JP 2005537324	T	20051208	JP 2004-533050	20030903
	US 20060008491	A1	20060112	US 2005-526692	20050804
PRAI	US 2002-408129P	P	20020903		
	WO 2003-AU1133	W	20030903		

OS MARPAT 140:248749
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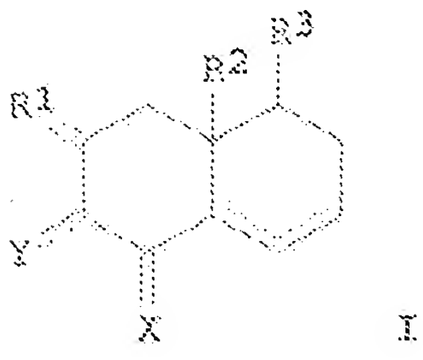


I

AB Eremophilone and derivs. I [X = O,S or NR4; Y = H,O, (CR52)nhalo, etc.; n = 0, 1-5; R1 = H, OH, SH, alkyl, alkenyl, alkynyl, etc.; R2, R3 = H, OH, SH, alkyl, alkenyl, alkynyl, aryl, arylalkyl, etc.; R4 = H, OH, alkyl,

etc.; R5 = H, halo, OH, etc.] are isolated as insecticides from Myoporaceae, such as Eremophila. I are especially active against termites and wood-boring beetles.

RE.CNT 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 6 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1997:277877 CAPLUS
DN 127:2987
OREF 127:683a,686a
TI (-)-1(10),11-eremophiladien-9β-ol from the liverwort Marchantia polymorpha ssp. aquatica
AU Rieck, Angela; Bulow, Nils; Fricke, Christiane; Saritas, Yucel; Konig, Wilfried A.
CS Inst. Org. Chem., Univ. Hamburg, Hamburg, D-20146, Germany
SO Phytochemistry (1997), 45(1), 195-197
CODEN: PYTCAS; ISSN: 0031-9422
PB Elsevier
DT Journal
LA English
AB A new eremophilane-type sesquiterpenoid, (-)-1(10),11-eremophiladien-9β-ol, was isolated from the liverwort Marchantia polymorpha ssp. aquatica. Structure elucidation was performed by means of spectroscopic methods and chemical conversion to known eremophilone. The configuration was proved by NOE measurements and comparison of the products obtained by dehydration and hydrogenation of the alc. with the hydrogenation products of both enantiomers of eremophilene and valencene by enantioselective gas chromatog. with cyclodextrin derivs.

RE.CNT 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

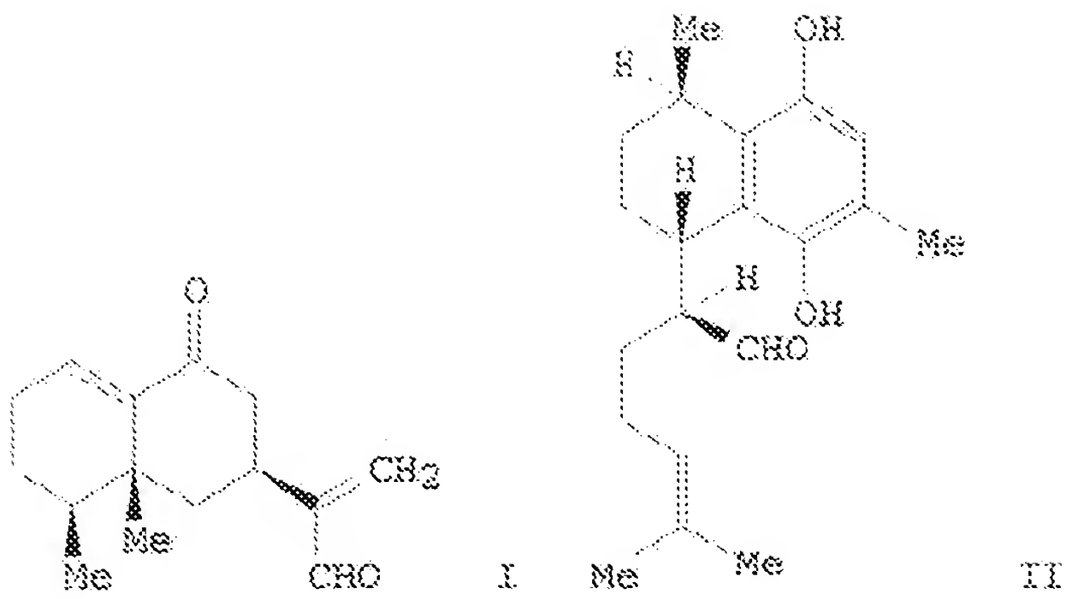
L4 ANSWER 7 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1996:2700 CAPLUS
DN 124:82106
OREF 124:15297a,15300a
TI Regeneration of plants and production of volatiles from callus cultures of Melissa officinalis L. 2. Root cultures: Growth and accumulation of volatiles
AU Van Den Berg, Thomas; Abou-Mandour, Ahmed A.; Czygan, Franz-C.
CS Julius-von-Sachs Institut fur Biowissenschaften, Universitat Wurzburg, Germany
SO Angewandte Botanik (1995), 69(3/4), 140-4
CODEN: ANBTAJ; ISSN: 0066-1759
PB Vereinigung fuer Angewandte Botanik
DT Journal
LA English
AB Root cultures obtained from callus of Lemon Balm (Melissa officinalis L., Lamiaceae) were cultivated under in-vitro conditions. Subsequently the volatiles obtained by hydrodistn. were analyzed qual. (GC/MS) and quant. During the 1st 70 days the root cultures exhibit a 4-fold increase of dry weight, but a 6-fold increase of volatiles. In older roots a slight decrease of the complex mixture was observed Among the 30 identified and quantified components eremophilene shows a special accumulation pattern, i.e. an earlier maximum and significant loss before 70 days. Two isomers of 2,3-dimethylcyclohexanone were detected in a fixed ratio. Concerning amount and composition of volatiles (hexanal, 2-pentylfuran, 2,3-dimethylcyclohexanone, eremophilene, dehydroabietane), the root cultures were very similar to callus cultures of Melissa. Compared with roots of intact plants a significant lack of monoterpenoids in root cultures is evident. Therefore contact to shoot of the plant might be necessary for accumulating monoterpenoids in the roots of this Labiate.

L4 ANSWER 8 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN

AN 1987:30044 CAPLUS
DN 106:30044
OREF 106:5003a,5006a
TI Components of further Compositae from Mongolia
AU Huneck, S.; Knapp, H. D.
CS Inst. Biochem. Pflanz., Dtsch. Akad. Wiss., Halle/Saale, Ger. Dem. Rep.
SO Pharmazie (1986), 41(9), 673
CODEN: PHARAT; ISSN: 0031-7144
DT Journal
LA German
AB Seven species of the Compositae of Mongolia (Galatella dahurica, Heteropappus biennis, Leontopodium ochroleucum campestre, Rhaponticum uniflorum, Saussurea parviflora, Senecio campestor, and Solidago dahurica) were investigated. Organic exts. of the above-ground plant parts were chromatographed on Kieselgel and isolated components identified by spectroscopic means. A variety of compds. were identified, including a number of terpenoids.

L4 ANSWER 9 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1986:606266 CAPLUS
DN 105:206266
OREF 105:33213a,33216a
TI Sesquiterpenes with new carbon skeletons. Furoeremophilanes, secoeremophilanes, and other constituents from Argentinian Senecio species
AU Bohlmann, F.; Jakupovic, J.; Warning, U.; Grenz, M.; Chau-Thi, T. V.; King, R. M.; Robinson, H.
CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, D-1000, Fed. Rep. Ger.
SO Bulletin des Societes Chimiques Belges (1986), 95(9-10), 707-36
CODEN: BSCBAG; ISSN: 0037-9646
DT Journal
LA English
AB Investigation of 10 Senecio species afforded 24 new furanoeremophilanes, 18 eremophilanolides, 7 seco- and 2 rearranged eremophilanolides, 12 bisabolone derivs. and 6 sesquiterpenes with new C skeletons which are most likely derived from the latter. Possible biogenetic pathways are discussed. Furthermore, 5 new eremophilones, an eudesmane, 4 p-hydroxyacetophenones, bis-coniferyl alc. derivs. and 5 shikimic acid derivs. were isolated. The structures were elucidated by using high-field NMR techniques and other spectroscopic methods.

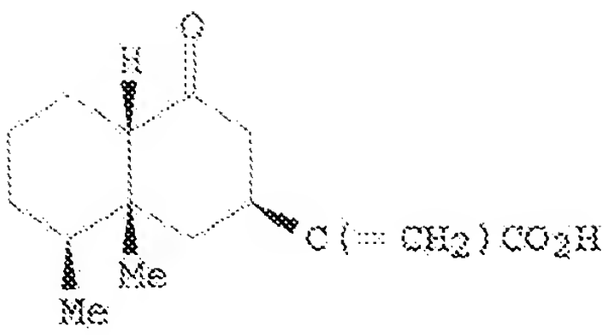
L4 ANSWER 10 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1985:611133 CAPLUS
DN 103:211133
OREF 103:33997a,34000a
TI Eremophilane and serrulatane terpenoids from Eremophila rotundifolia
AU Abell, Andrew D.; Massy-Westropp, Ralph A.
CS Dep. Org. Chem., Univ. Adelaide, Adelaide, 5001, Australia
SO Australian Journal of Chemistry (1985), 38(8), 1263-9
CODEN: AJCHAS; ISSN: 0004-9425
DT Journal
LA English
GI



AB The new terpenoids 9-oxoeremophila-10,11(13)-dien-12-al (I) and 5,8-dihydroxyserrulat-14-en-18-al (II) were isolated from E. rotundifolia. Their absolute stereochem. was established by chemical correlation with known compds.

L4 ANSWER 11 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1984:197640 CAPLUS
DN 100:197640
OREF 100:29961a,29964a
TI GC-MS analysis of essential oil of Rhododendron dauricum L
AU Ma, Yaping; Sun, Shouwei; Wu, Chengshun
CS Natl. Inst. Metrol., Peop. Rep. China
SO Zhiwu Xuebao (1983), 25(6), 563-7
CODEN: CHWHAY; ISSN: 0577-7496
DT Journal
LA Chinese
AB R. dauricum (A medicinal plant) leaf oil contained α-pinene [80-56-8], camphene [79-92-5], β-pinene [127-91-3], limonene [138-86-3], cyclofenchene [488-97-1], 1-methyl-2-isopropylbenzene [527-84-4], 3-methylbutyl isovalerate [659-70-1], α-copaene [3856-25-5], (1α,3aα,3bα,6aβ,6bα)-decahydro-3a-methyl-6-methylene-1-(1-methylethyl)cyclobuta[1,2:3,4]dicyclopentane [5208-59-3], bornyl acetate [76-49-3], cis-4,11,11-trimethyl-8-methylenebicyclo[7.2.0]undec-4-ene [89575-63-3], δ-guaiene [3691-11-0], γ-muurolene [30021-74-0], β-maaliene [489-29-2], eremophilone [562-23-2], α-muurolene [10208-80-7], δ-cadinene [483-76-1], γ-cadinene [39029-41-9], γ-selinene [515-17-3], 4,10-dimethyl-7-isopropylbicyclo[4.4.0]-1,4-decadiene [16728-99-7], γ-elemene [29873-99-2], germacrone [6902-91-6], juniper camphor [473-04-1] and β-selinene [17066-67-0] as determined by gas chromatog.-mass spectroscopy (GC-MS).

L4 ANSWER 12 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1983:215816 CAPLUS
DN 98:215816
OREF 98:32825a,32828a
TI Synthetic studies in the eremophilane sesquiterpene group. Synthesis of fluorensic acid
AU Herron, Joe N.; Pinder, A. Reginald
CS Dep. Chem., Clemson Univ., Clemson, SC, 29631, USA
SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1983), (1), 161-6
CODEN: JCPRB4; ISSN: 0300-922X
DT Journal
LA English
GI



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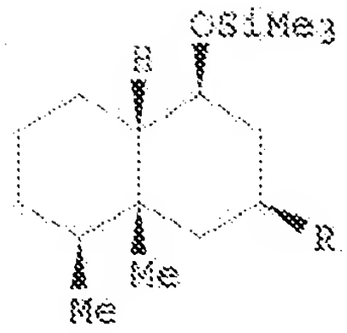
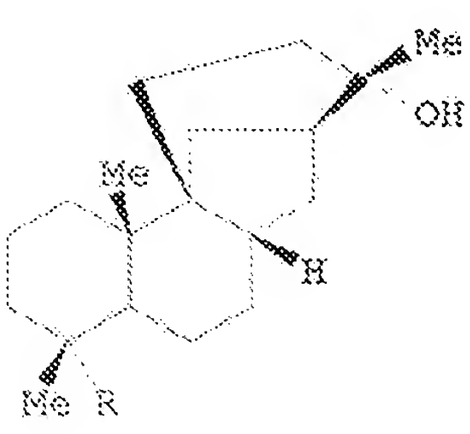


II

AB (+)-Fluorensic acid (I) was prepared from eremophilone in 8 steps. A key step was the Wittig-Horner reaction of the ketone II (R = COMe) with Ph2P(O)CH2OMe to give the enol ether II (R = CMe:CHOMe) in 78% yield.

L4 ANSWER 13 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1983:198477 CAPLUS
DN 98:198477
OREF 98:30183a,30186a
TI Total synthesis of the stemodane-type diterpenoids, (±)-2-deoxystemodinone, (+)-2-deoxystemodinone, and (±)-stemodinol
AU Kelly, Ronald B.; Harley, Mary Lou; Alward, Sandra J.; Rej, Rabindra N.; Gowda, Gopala; Mukhopadhyay, Asish; Manchand, Percy S.
CS Dep. Chem., Univ. New Brunswick, Saint John, NB, E2L 4L5, Can.
SO Canadian Journal of Chemistry (1983), 61(2), 269-75
CODEN: CJCHAG; ISSN: 0008-4042
DT Journal
LA English
GI



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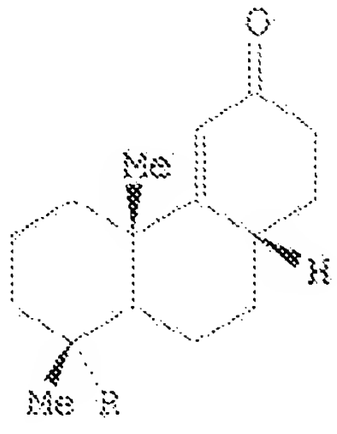
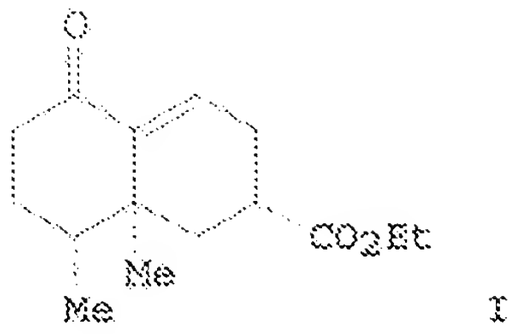


II

AB Stereospecific total syntheses of (±)-2-deoxystemodinone (I, R = Me), (+)-2-deoxystemodinone, and (±)-stemodinol (I, R = CH2OH) from II (R = Me, CO2Me) are described. (+)-2-Deoxystemodinone was isolated from Stemodia maritima and characterized. A strategy for the elaboration of the C/D ring systems of the stemodane diterpenoids, stemarin and aphidicolin, from a common 6-hydroxybicyclo[2.2.2]octan-2-one system is outlined and its usefulness is demonstrated.

L4 ANSWER 14 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1983:143668 CAPLUS
DN 98:143668
OREF 98:21897a,21900a
TI A stereocontrolled entry to racemic eremophilane and valencane sesquiterpenes via an intramolecular Diels-Alder reaction
AU Naef, Ferdinand; Decorzant, Rene; Thommen, Walter
CS Res. Lab., Firmenich SA, Geneva, CH-1211/8, Switz.
SO Helvetica Chimica Acta (1982), 65(7), 2212-23
CODEN: HCACAV; ISSN: 0018-019X
DT Journal
LA English

GI



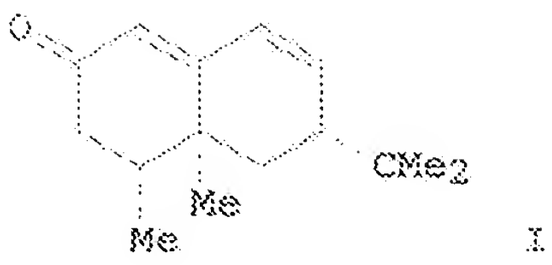
I

AB Eremophilane and valencane sesquiterpenes were prepared via I, which was prepared by intramol. Diels-Alder reaction of H2C:CMeCHMeCH2CH2COCH:CHCH:CHCO2Et, prepared by condensing H2C:CMeCHMeCH2CH2COMe with Et oxobutenoate.

L4 ANSWER 15 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1978:121438 CAPLUS
DN 88:121438
OREF 88:19069a,19072a
TI The total synthesis of eremophilone, Part I. Approaches to the synthesis of aphidicolin, Part II
AU Musser, John Henry
CS Univ. California, Santa Cruz, CA, USA
SO (1976) 126 pp. Avail.: Univ. Microfilms Int., Order No. 77-16,797
From: Diss. Abstr. Int. B 1977, 38(2), 695-6
DT Dissertation
LA English
AB Unavailable

L4 ANSWER 16 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1977:601809 CAPLUS
DN 87:201809
OREF 87:31959a,31962a
TI The total synthesis of eremophilone, part I. Approaches to the synthesis of aphidicolin, part II
AU Musser, John Henry
CS Univ. California, Santa Cruz, CA, USA
SO (1976) 126 pp. Avail.: Univ. Microfilms Int., Order No. 77-16,797
From: Diss. Abstr. Int. B 1977, 38(2), 695-6
DT Dissertation
LA English
AB Unavailable

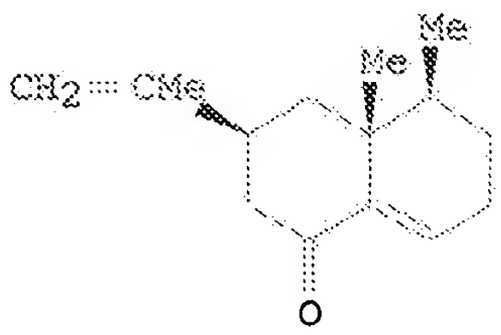
L4 ANSWER 17 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1977:601791 CAPLUS
DN 87:201791
OREF 87:31955a,31958a
TI Further studies relating to the structure of nardostachone
AU Saunders, W. D.; Pinder, A. R.
CS Dep. Chem., Clemson Univ., Clemson, SC, USA
SO Tetrahedron Letters (1977), (20), 1687-90
CODEN: TELEAY; ISSN: 0040-4039
DT Journal
LA English
GI



I

AB Nardostachone, a constituent of Indian spikenard oil, was previously assigned structure I by W. M. B. Koenst et al. (1975). Preparation of I, by annulation of cis-4-isopropenyl-2-methylcyclohexanone with trans-MeCH:CHCOMe followed by treatment with dilute mineral acid at 55-65°, and comparison of spectral data showed that nardostachone is not I.

L4 ANSWER 18 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1977:502447 CAPLUS
DN 87:102447
OREF 87:16275a,16278a
TI Stereoselective total synthesis of (±) eremophilone
AU Ficini, Jacqueline; Touzin, Anne M.
CS Lab. Chim. Org. Synth., Univ. Pierre Marie Curie, Paris, Fr
SO Tetrahedron Letters (1977), (12), 1081-4
CODEN: TELEAY; ISSN: 0040-4039
DT Journal
LA English
GI



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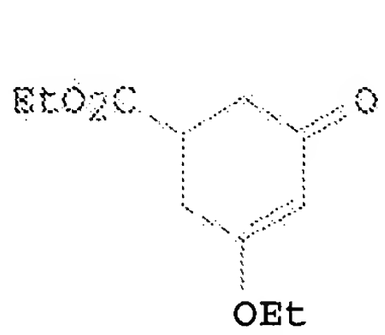
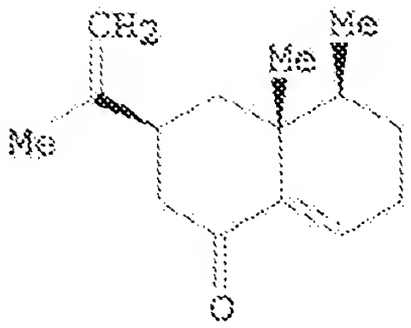


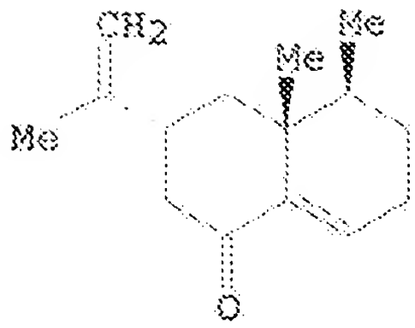
II

AB (±)-Eremophilone (I) was prepared stereoselectively in 12 steps from the cyclohexenone II. (±)-Dihydroeremophilone was prepared in 8 and 10 steps from II.

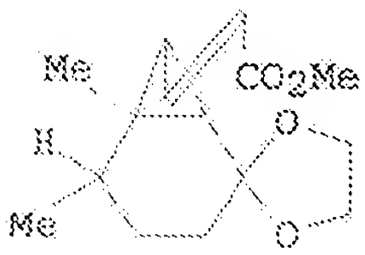
L4 ANSWER 19 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1977:423527 CAPLUS
DN 87:23527
OREF 87:3733a,3736a
TI Stereochemistry of dialkylcuprate additions to cyclopropyl acrylic esters. An application to the synthesis of (±)-eremophilone
AU Ziegler, Frederick E.; Reid, Gary R.; Studt, William L.; Wender, Paul A.
CS Sterling Chem. Lab., Yale Univ., New Haven, CT, USA
SO Journal of Organic Chemistry (1977), 42(11), 1991-2001
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA English
GI



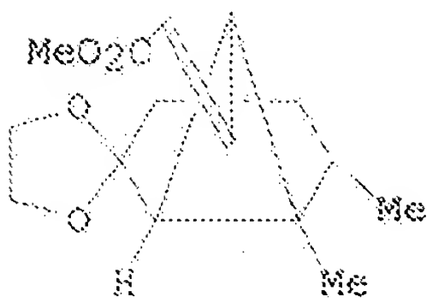
I



II



III



IV

AB The total synthesis of eremophilone (I) and its C-7 epimer II are discussed. The vicinal arrangement of cis-dimethyl groups was achieved by the stereocontrolled addition of Li divinylcuprate to 3,4-dimethylcyclohex-2-en-1-one. The C-7 center was created in a stereorandom fashion via a Claisen rearrangement one carbon removed from the nearest asymmetric site. This problem was solved in part by examining the stereochem. of the addition of Li diisopropenylcuprate to syn and anti cyclopropylacrylic esters III and IV resp. The C-7 stereochem. of the addition in the syn series was shown to favor the eremophilone stereochem. (98/2) while the addition in the anti series was (85/15) in favor of the epieremophilone stereochem.

L4 ANSWER 20 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1975:443513 CAPLUS
DN 83:43513
OREF 83:6898h,6899a
TI Interconversion of eremophilone and isoeremophilone and related reactions
AU Zalkow, Leon H.; Chetty, G. L.
CS Sch. Chem., Georgia Inst. Technol., Atlanta, GA, USA
SO Journal of Organic Chemistry (1975), 40(12), 1833-4
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB Quenching of the enolate of eremophilone gave isoeremophilone. Equilibration of these 2 ketones led to a .apprx.1:1 mixture of I and II. Reduction of I with LiAlH4/AlCl3 (1:2) gave III, an isomer of eremophilene. Similarly eremophilone was converted into IV, an isomer of eremoligenol (V).

L4 ANSWER 21 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1975:443512 CAPLUS
DN 83:43512
OREF 83:6895a,6898a
TI Total synthesis of eremophilone
AU McMurry, John E.; Musser, John H.; Ahmad, Mohammed S.; Blaszczak, Larry C.
CS Thimann Lab., Univ. California, Santa Cruz, CA, USA
SO Journal of Organic Chemistry (1975), 40(12), 1829-32
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB A stereoselective total synthesis of (±)-eremophilone is reported starting from the known 7-epinootkatone. The synthetic sequence involves reductive deconjugation of 7-epinootkatone to homoallylic alc. I. Dehydration of I by pyrolysis of its acetate gave triene II which can be

selectively epoxidized at the more substituted double bond to give III. Mild acid catalyzed rearrangement of this allyltic epoxide with LiClO4 in refluxing benzene gave, after base catalyzed equilibration of the enone system, a 1:1 mixture of eremophilone and its β,γ-unsatd. isomer, itself a natural product.

L4 ANSWER 22 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1974:463799 CAPLUS
DN 81:63799
OREF 81:10173a,10176a
TI Stereospecific generation of the cis-vicinal methyls in eremophilane and valencane sesquiterpenes. Total synthesis of (+-)-eremophilone and (+-)-7-epieremophilone
AU Ziegler, Frederick E.; Wender, Paul A.
CS Sterling Chem. Lab., Yale Univ., New Haven, CT, USA
SO Tetrahedron Letters (1974), (5), 449-52
CODEN: TELEAY; ISSN: 0040-4039
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB The title compds. (I and II) were prepared from 3,4-dimethylcyclohex-2-en-1-one. Successive stereospecific vinylation, ketalization, hydroboration, CrO3 oxidation, and reflux in C6H6, gave the ester III. Successive LiAlH4 reduction, BuOCH: CH2 treatment, and hydrolysis of III gave IV. Ring closure of IV gave an enon, Wharton reaction of which gave II, and a β-hydroxyketone, pyrolysis and Wharton reaction of which gave I.

L4 ANSWER 23 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1974:449873 CAPLUS
DN 81:49873
OREF 81:7967a,7970a
TI Transformation of ketones into nitriles. Total synthesis of eremophilone
AU Wender, Paul A.
CS Yale Univ., New Haven, CT, USA
SO (1973) 205 pp. Avail.: Univ. Microfilms, Ann Arbor, Mich., Order No. 74-11,911
From: Diss. Abstr. Int. B 1974, 34(11), 5395
DT Dissertation
LA English
AB Unavailable

L4 ANSWER 24 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1971:63285 CAPLUS
DN 74:63285
OREF 74:10217a,10220a
TI Odor character and threshold values of nootkatone and related compounds
AU Stevens, Kenneth L.; Guadagni, Dante G.; Stern, Donald J.
CS West. Util. Res. Dev. Div., U. S. Dep. Agric., Albany, CA, USA
SO Journal of the Science of Food and Agriculture (1970), 21(11), 590-3
CODEN: JSFAAE; ISSN: 0022-5142
DT Journal
LA English
AB The odor character and potency of nootkatone obtained from grapefruit oil were compared with those of some closely related compds. These compds. may differ considerably in qual. but the potency remains similar. In addition, synthesized racemic nootkatone had the same potency as the naturally occurring material.

L4 ANSWER 25 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1969:502047 CAPLUS
DN 71:102047
OREF 71:19021a,19024a
TI Terpenoids. XV. α-vetivone

AU Endo, Katsuya; De Mayo, Paul
CS Univ. Western Ontario, London, ON, Can.
SO Chemical & Pharmaceutical Bulletin (1969), 17(7), 1324-31
CODEN: CPBTAL; ISSN: 0009-2363
DT Journal
LA English
OS CASREACT 71:102047
GI For diagram(s), see printed CA Issue.
AB The structure of α-vetivone (I) one of the major odoriferous principles of vetiver oil was reexamd. Air oxidation of I in the presence of N tert-BuOK yielded, after treatment with p-toluenesulfonic acid, a conjugated dienedione. The enantiomeric compound was prepared by oxidation, of the structurally well-established eremophilone, thus requiring that the structure of I be described as shown. Some interesting observations were made with regards O.R.D. and circular dichroism measurements in comparison with curves obtained from cholest-4-en-3-one. Biogenetic relations between some related compds. are also discussed.

L4 ANSWER 26 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1967:500360 CAPLUS
DN 67:100360
OREF 67:18907a,18910a
TI Synthesis of conformationally stable carbohydrates. Studies on synthetic sesquiterpenes related to eremophilone
AU Piszkiewicz, Leonard W.
CS California Inst. of Technol., Pasadena, CA, USA
SO (1967) 152 pp. Avail.: 67-6068
From: Diss. Abstr. B 1967, 27(11), 3865
DT Dissertation
LA English
AB Unavailable

L4 ANSWER 27 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1967:422036 CAPLUS
DN 67:22036
OREF 67:4215a,4218a
TI A selective reduction using tris(triphenylphosphine)-chlororhodium I
AU Brown, Morris; Piszkiewicz, Leonard W.
CS Calif. Inst. of Technol., Pasadena, CA, USA
SO Journal of Organic Chemistry (1967), 32(6), 2013-14
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA English
OS CASREACT 67:22036
GI For diagram(s), see printed CA Issue.
AB Eremophilone (I) is hydrogenated in the presence of the title Rh compound to give 13,14-dihydroeremophilone (II). Eremophilone oxide (III), m. 60-1°, (2.16 g.) is hydrogenated in the presence of 0.05 g. 5% Pd/C to give 95% dihydroeremophilone oxide (IV), m. 50-1°; N.M.R. data for III and IV are given. A solution of 2 g. of IV in 40 ml. HOAc is agitated under N as 60 ml. 0.5M $CrCl_2$ is added; the mixture is agitated 2.5 hrs. and added to water to give 85% II, b. 100° [sic], n25 1.5015, [α]D -175° (c 0.411, MeOH). A solution of 0.102 g. I and 0.07 g. tris(triphenylphosphine)chlororhodium-(I) in 15 ml. C_6H_6 is agitated 8 hrs. under H to give 94% II. Uv spectral data for the compds. prepared are given.

L4 ANSWER 28 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1967:85869 CAPLUS
DN 66:85869
OREF 66:16087a,16090a
TI Eremophilone and alloeremophilone from hydroxydihydroeremophilone
AU Bates, Robert B.; Paknikar, S. K.
CS Univ. of Arizona, Tucson, AZ, USA

SO Chemistry & Industry (London, United Kingdom) (1966), (52), 2170-1
CODEN: CHINAG; ISSN: 0009-3068
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB Acetoxydihydroeremophilone pyrolyzed 5 min. at 270-300° afforded, after extractive work up, a 53.5/46.5 mixture of eremophilone and a new ketone alloeremophilone (I), in 80% yield. Structure I was assigned to the new compound as a result of its method of formation and its N.M.R. spectrum. A mechanism is proposed which accounts for the products formed.

L4 ANSWER 29 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1963:4500 CAPLUS
DN 58:4500
OREF 58:749h
TI Plant substances. XIX. The constituents of Petasites spurius rhizomes
AU Novotny, L.; Herout, V.
CS Ustav Org. Chemic, Csl. Akad. Ved, Prague
SO Collection of Czechoslovak Chemical Communications (1962), 27, 2462-4
CODEN: CCCCAK; ISSN: 0010-0765
DT Journal
LA Unavailable
AB Light petr. ether extract of 800 g. dried rhizomes of P. spurius gave, in addition to sesquiterpenic hydrocarbons identified by gas-liquid chromatography, 2.9 g. albopetasin, m. 106-7° (iso-Pr2O), and 7.8 g. petasalbin, m. 80-1° (iso-Pr2O), [α]20D -11.0°.

L4 ANSWER 30 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1961:37968 CAPLUS
DN 55:37968
OREF 55:7370c-i,7371a-i
TI Terpenoids. XLVIII. The absolute configuration of eremophilone and related sesquiterpenes
AU Zalkow, Leon H.; Markley, F. X.; Djerassi, Carl
CS Wayne State Univ., Detroit, MI
SO Journal of the American Chemical Society (1960), 82, 6354-62
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
OS CASREACT 55:37968
GI For diagram(s), see printed CA Issue.
AB cf. CA 55, 2723i. The absolute configurations of eremophilone, hydroxydihydro-, and hydroxyeremophilone (I) were established by the synthesis of the common degradation product, trans-5,10-dimethyl-3α-isopropyl-2-decalone (II) from an intermediate of known absolute configuration. Judging from rotatory dispersion evidence, the CO-containing ring of eremophilone did not exist in a chair conformation. Attention was also directed to the demethoxylation of α-methoxy ketones with Ca in liquid NH3.
(+)-trans-3-Methoxy-9-methyl-Δ2,6-hexal-1-one (9.4 g.) in 100 cc. dry Et2O added dropwise to MeLi from 1.6 g. Li and 6.5 g. MeI in 100 cc. Et2O under N, stirred 12 hrs. at room temperature, poured into iced H2O, and worked up, the viscous oily residue stirred 3 hrs. with 35 cc. concentrated H2SO4, 250 cc. H2O, and 300 cc. dioxane, and the product isolated with Et2O yielded 6.8 g. (+)-trans-4,10-dimethyl-Δ3,6-hexal-2-one (III), prisms, m. 42-4° (hexane), [α]589 295° (c 0.155, dioxane); semicarbazone, m. 171-3° (aqueous EtOH); 2,4-dinitrophenylhydrazone, red, m. 173-5° (aqueous iso-PrOH). III (8.15 g.) in 150 cc. 2% alc. KOH hydrogenated 10 hrs. under ambient conditions over 1.0 g. 2% Pd-CaCO3 yielded 6.64 g. (+)-trans-4,10-dimethyl-Δ6-octal-2-one (IV), b1.5 110-11°, [α]589 33° (c 0.083, MeOH); semicarbazone, m. 210-12° (decomposition) (aqueous EtOH). III (973 mg.) in 50 cc. absolute EtOH treated with 5

g. Na in small pieces, refluxed 1 hr., diluted with H2O, and extracted with Et2O gave 712 mg. trans-4,10-dimethyl-Δ6-octal-2-ol (V), b0.05 80° (bath). V (515 mg.) in 25 cc. AcOH treated 1 hr. at room temperature with 250 mg. CrO3 in 30 cc. 80% AcOH yielded 400 mg. IV, b0.4 70°. III or IV in MeOH hydrogenated over 5% Pd-C, and the resulting mixture shaken 1 hr. with 50 cc. 1:1 3N HCl-dioxane, diluted with H2O, and extracted with Et2O gave (-)-trans-4,10-dimethyl-decal-2-one (VI), b0.5 70-3°, [α]589 -83°, -22° after the addition of 1 drop concentrated HCl. VI (80 mg.) treated at room temperature with 150 mg. 2,4-(O2N)2C6H3NHNH2 gave the 2,4-dinitrophenylhydrazone, orange-yellow needles, m. 136-8° (MeOH). IV (5.67 g.), 6 cc. 85% N2H4.H2O, 5.1 g. KOH, and 50 cc. (HOCH2CH2)2O refluxed 1.5 hrs., distilled up to 200°, refluxed 7 hrs., and worked up gave 4.27 g. (+)-trans-1,9-dimethyl-Δ6-octahydronaphthalene (VII), b28 110-11°, [α]589 50° (c 0.064, MeOH). N-Bromosuccinimide (5.2 g.) added slowly during 0.5 hr. to 3.55 g. VII in 150 cc. Me3COH and 45 cc. N H2SO4, kept 5 hrs. at room temperature, and diluted with H2O, and the product isolated with Et2O gave 3.26 g. viscous oil, b0.005 90-100°, consisting mostly of (+)-trans-5,10-dimethyl-2α-bromo-3β-decalol (VIII) with a small amount of (+)-trans-5,10-dimethyl-3α-bromo-2β-decalol (IX). VIII-IX mixture (2.54 g.) in 125 cc. glacial AcOH treated 1 hr. with 0.67 g. CrO3 in aqueous AcOH, diluted with H2O, and extracted with Et2O gave 1.884 g. distillate, b0.007 85-90°, which deposited on standing several days 81 mg. (+)-trans-5,10-dimethyl-3α-bromodecal-2-one (X), m. 155-7° (sublimed at 110°/0.3 mm.); the filtrate yielded the liquid (+)-trans-8,9-dimethyl-3α-bromodecalone (XI). XI (813 mg.) in 8 cc. AcOH containing 2 drops H2O warmed 15 min. with stirring at 60° with 813 mg. Zn dust, diluted with H2O, and extracted with Et2O yielded 335 mg. (+)-trans-8,9-dimethyl-2-decalone (XII), b1 100-5°. XI (140 mg.) in 10 cc. Me2CO treated with a CrCl2 solution from 2.5 g. CrCl3 and worked up gave 80 mg. XII, b0.3 80-90°; 2,4-dinitrophenylhydrazone, yellow, m. 140.5-1.5° (MeOH). X (25 mg.), 2 cc. glacial AcOH containing 1 drop H2O, and 25 mg. Zn dust heated 5 min. on the steam bath and diluted with H2O, and the product isolated with Et2O and treated with 2,4-(O2N)2C6H3NHNH2 gave 17 mg. 2,4-dinitrophenylhydrazone of (+) trans-5,10 dimethyl-2-decalone (XIII), m. 172.5-3.5° (MeOH). VII (345 mg.) in 50 cc. CHCl3 and 3.7 millimoles BzO2H kept 19 hrs. at room temperature yielded 320 mg. epoxide (XIV) of VII, b15 120-30°. XIV (300 mg.) in 25 cc. Et2O reduced during 20 hrs. with 0.4 g. LiAlH4 in 75 cc. Et2O yielded 220 mg. (+)-trans-5,10-dimethyl-2α-decalol (XV), b1.5 115-20°. XV (200 mg.) in AcOH treated 0.5 hr. at room temperature with 100 mg. CrO3 yielded 140 mg. XIII, m. 29-30°; 2,4-dinitrophenylhydrazone, yellow, m. 172.5-3.5° (MeOH). XIII (850 mg.) and 520 mg. NaH in 20 cc. dry C6H6 stirred 17 hrs. under N with 1.8 cc. (CO2Et)2 and worked up, and the product isolated with Et2O yielded 1.17 g. 3α-EtO2CCO analog (XVI) of X, b0.7 90-100°. The XVI and powdered soft glass distilled at 30 mm. gave 72% 3α-EtO2C analog (XVII) of X, b0.01 65°. XVII (3.39 g.), 1 cc. (CH2OH)2, 10 cc. dry C6H6, and a few crystals p-MeC6H4SO3H azeotroped 15 hrs., diluted with Et2O, and worked up gave 3.0 g. cycloethylene ketal (XVIII) of XVII, b0.01 80-90°. XVIII (2.84 g.) in 10 cc. dry Et2O added dropwise to MeMgI from 1.55 cc. MeI, 0.61 g. Mg, and 10 cc. Et2O, refluxed 3 hrs., and worked up gave 2.46 g. 3α-Me2(HO)C analog (XIX) of X, b0.005 80-100°, m. 55-60°. XIX (2.01 g.), 8 cc. POCl3, and 17 cc. C5H5N kept overnight and poured into 2 l. iced H2O, and the product isolated with Et2O and chromatographed on Al2O3 yielded 1.63 g. 3α-CH2:CMe analog (XX) of X, b0.1 90-105°, [α]589 4° (c 0.35, MeOH). XX (756 mg.) in 20 cc. EtOAc hydrogenated 2 hrs. over 80 mg. 10% Pd-C gave 3α-iso-Pr analog (XXI) of X, b0.1 80-90°, [α]589 -25° (c 2.32, MeOH). XXI (470 mg.), 12 cc. MeOH, 2 cc. H2O, and 2 drops concentrated HCl stirred overnight, diluted with H2O, and extracted with Et2O

yielded oily II, b0.01 60-70°, [α]589 -15° (c 0.21, MeOH); 2,4-dinitrophenylhydrazone, m. 169-72° (pentane); semicarbazone, m. 176-80° (aqueous EtOH and sublimed at 0.1 mm.). XIX (2.2 g.), 15 cc. MeOH, 10 cc. H2O, 5 drops concentrated HCl, refluxed 1 hr., and partitioned between H2O and Et2O, and the Et2O phase worked up gave 1.42 g. oil, b0.04 60°; a 1.41-g. portion in 20 cc. C5H5N and 5 cc. POCl3 heated 1 hr. on the steam bath, diluted with H2O, and extracted with Et2O gave 392 mg. crude oily XIII; the aqueous C5H5N layer acidified with 3% HCl and extracted with Et2O gave 562 mg. trans-5,10-dimethyl-3-isopropylidene-2-decalone (XXII), b0.01 70-80°. XXII (426 mg.) hydrogenated in 40 cc. EtOH at 28° over 150 mg. 10% Pd-C yielded 300 mg. 3β-iso-Pr analog of XXII, b0.01 70°, [α]589 67° (c 0.116, MeOH); 2,4-dinitrophenylhydrazone, yellow, m. 170.5-2.5° (pentane). I (2.02 g.) with Me2SO4 yielded 2.17 g. Me ether (XXIII) of I, b0.01 80°, [α]589 177° (c 0.095, dioxane). XXIII (551 mg.) in 20 cc. EtOH hydrogenated 1.5 hrs. under ambient conditions over 90 mg. 10% Pd-C gave 485 mg. tetrahydro derivative (XXIV) of XXIII, b0.1 65-70°, [α]589 130° (c 0.285, MeOH). XXIX (170 mg.) refluxed 5 hrs. under N with 12 cc. N NaOH-MeOH yielded 140 mg. epi-XXIV (XXV), b0.01 60-70°, [α]589 -67°. XXV (3.02 g.) chromatographed on 150 g. Al2O3 yielded 1.28 g. pure XXV. XXV (1.08 g.) in 10 cc. dioxane added dropwise to 1.5 g. Ca in 150 cc. liquid NH3, refluxed 1 hr., and evaporated overnight, and the residue treated with saturated aqueous NH4Cl and worked up gave 937 mg. XXVI, b0.05 70-80°, which oxidized in AcOH with 0.4 g. CrO3 and worked up in the usual manner gave the 3α-iso-Pr analog of XXII; semicarbazone, m. 178-81°.

L4 ANSWER 31 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1961:6256 CAPLUS
DN 55:6256
OREF 55:1184g-i
TI Stereochemistry and infrared spectra of α,β-unsaturated ketones
AU Erskine, R. L.; Waight, E. S.
CS Imp. Coll. Sci. and Technol., London
SO Journal of the Chemical Society (1960) 3425-31
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable
AB The infrared spectra of some polycyclic rigidly cisoid α,β-unsatd. ketones have been determined These show absorption bands attributable to C:O and C:C stretching vibrations which are of nearly equal peak height. In rigidly transoid systems, the C:O band is much more intense. Thus, the ratio of the integrated band intensities of the C:O and C:C stretching vibrations gives the most certain indication of the geometry of the chromophore. The effect of steric hindrance to coplanarity of the chromophore on the infrared spectra is discussed.

L4 ANSWER 32 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1960:7439 CAPLUS
DN 54:7439
OREF 54:1590a-i,1591a-g
TI Terpenoids. XXXVIII. Interconversion of eremophilone, hydroxyeremophilone, and hydroxydihydroeremophilone. Relative stereochemistry of eremophilone and its reduction products
AU Djerassi, Carl; Mauli, R.; Zalkow, Leon H.
CS Wayne State Univ., Detroit, MI
SO Journal of the American Chemical Society (1959), 81, 3424-9
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
OS CASREACT 54:7439
AB cf. C.A. 53, 22060a. The present paper is concerned with the determination of the

relative configuration of eremophilone (I) and several of its reduction products, in order to devise a stereochem. unambiguous synthesis of I. Hydroxydihydroeremophilone (II) [m. 99-102°, λ (EtOH) 281 mμ (log ε 2.54), λ (MeOH) 281 mμ (log ε 2.50), λ (dioxane) 281 mμ (log ε 2.50)] (236 mg.) in 2 cc. C5H5N and 1 cc. Ac2O heated 2.5 hrs. on the steam bath, poured into H2O, extracted with CHCl3, the extract washed with dilute acid, base, and H2O, dried, evaporated, and the residue recrystd. twice from aqueous MeOH gave II acetate (III), m. 68-70°; anal. sample m. 68-70°, λ (CHCl3) 5.75, 5.80, 6.07, 7.95-8.00, 11.12 μ, λ (EtOH) 286 mμ (log ε 1.77), R.D. (rotatory dispersion) in MeOH [c 0.243 (700-305 mμ), 0.0486 (300-265 mμ)]: [α]700 82°, [α]589 120°, [α]335-40 369°, [α]310 206°, [α]273 1331°, [α]265 1034°. The identical reaction conducted 2 days in the refrigerator gave 192 mg. III. II (472 mg.) and 1.14 g. p-MeC6H4SO2Cl (IV) in 5 cc. C5H5N kept 2 days at room temperature, poured into ice-H2O, the precipitate collected, and recrystd. from MeOH and then aqueous MeOH gave II tosylate (V), m. 138-40°, R.D. in MeOH [c 0.258 (700-300 mμ), 0.0516 (295-275 mμ)]: [α]700 61°, [α]589 93°, [α]345-50 255°, [α]313 15°, [α]280 1240°, [α]275 -1255°. V (390 mg.) and 1.5 g. NaI in 20 cc. Me2CO heated 10 hrs. in a bomb at 100° and worked up gave a dienone contaminated with a product having a saturated carbonyl group. Hydrogenation of 472 mg. II at atmospheric pressure and 30° in 5 cc. EtOAc with 10% Pd-C (H absorption stopped after 15 min.), the solution filtered, the filtrate evaporated, and the residue recrystd. twice from aqueous MeOH gave 325 mg. hydroxytetrahydroeremophilone (VI), m. 84-5°, λ (EtOH) 281 mμ (log ε 1.77), R.D. in MeOH [c 0.246 (700-300 mμ), 0.0492 (295-270 mμ)]: [α]700 48°, [α]589 70°, [α]355-60 176°, [α]310 -114°, [α]278 963°, [α]270 590°. VI (2.0 g.) in 15 cc. C5H5N and 10 cc. Ac2O kept 2 days at 0° and worked up gave 2.23 g. acetate (VII), m. 51-3°; anal. sample m. 51-3°, λ (EtOH) 287 mμ (log ε 1.29), R.D. in MeOH [c 0.216 (700-292.5 mμ), 0.043 (290-257.5 mμ)]: [α]700 94°, [α]589 140°, [α]330-325 547°, [α]310 417°, [α]262.5 1797°, [α]257.5 1676°. III (43.4 mg.) hydrogenated in MeOH with 10% Pd-C, filtered, the filtrate concentrated to 0.5 cc., and a few drops of H2O added gave 37 mg. VII. VII did not form a 2,4-dinitrophenylhydrazone or semicarbazone. III (278 mg.) in PhMe added with vigorous stirring during 5 min. to 2.0 g. Ca dissolved in 50 cc. liquid NH3 at -33°, stirred 5 min. more, 2 cc. PhBr added followed by 10 cc. H2O, the NH3 allowed to evaporate during 3 hrs., the mixture concentrated in vacuo to near dryness, the residue partitioned between CHCl3 and HCl, the organic phase separated, washed, dried, and the residue distilled gave 80% cis-dihydroeremophilone (VIII), yellow oil, b0.01 110-40° (bath temperature), redistn. affording the analytical sample, λ (CHCl3) 5.83, 6.02, and 11.18 μ, identical with VIII derived from I, R.D. in MeOH [c 0.247 (700-320 mμ), 0.0494 (315-290 mμ), 0.0247 (285-275 mμ)]: [α]700 21°, [α]589 38°, [α]400-395 63°, [α]313 -372°, [α]275 1732°; 2,4-dinitrophenylhydrazone (IX), m. 173-4° (CH2Cl2-MeOH), identical with IX obtained from VIII derived from I. VII (1.39 g.) deacetoxylated as above with 10 g. Ca and 200 cc. liquid NH3 (15 min. for addition followed by 30 min. stirring) and the product distilled gave 0.95 g. cis-tetrahydroeremophilone (X), b0.005 110° (bath temperature), identical with X obtained by catalytic reduction of I followed by acid isomerization of the initially produced trans isomer; 2,4-dinitrophenylhydrazone (XI), m.p. and mixed m.p. 179-81°. VIII (32 mg.) reduced in EtOH with 10% Pd-C (97.8% H absorbed in 1 hr.) and the product distilled gave X. VI (238 mg.) reduced with 5 g. 4% Na-Hg (method of Bradfield, et al., C.A. 27,

497), the product (130 mg.) distilled, chromatographed on Al2O3, eluted with hexane, and the product distilled gave X; later eluates gave unreacted VI, m. 82-4°. VII (1.14 g.), 0.60 g. NaBH4, and 25 cc. MeOH kept 2.5 hrs. at room temperature, the MeOH distilled on the steam bath, the residual solution neutralized with aqueous HCl, extracted with Et2O, the product chromatographed on Al2O3, eluted 1st with C6H6-CHCl3 (the product from the eluate not further examined) and then C6H6, and the product distilled gave a hydroxy acetate compound (XII), b0.03 140-60° (bath temperature). A portion of XII heated 1 hr. on the steam bath in C5H5N with excess IV, the crude product chromatographed on Al2O3, eluted with C6H6 and 9:1 C6H6-CHCl3, and recrystd. from hexane gave the acetoxy tosylate compound (XIII), m. 129-31°. XIII (118 mg.) in 15 cc. Et2O added to 380 mg. LiAlH4 in 25 cc. Et2O, refluxed 30 min., excess LiAlH4 decomposed with EtOAc, HCl added, the product extracted with Et2O, the extract washed, dried, evaporated, and the residue distilled (0.01 mm.) gave 44 mg. oil, assumed to be cis-tetra-hydroeremophilol (XIV). XIV (44 mg.) oxidized with CrO3 in AcOH (15 min., room temperature) and the resulting product (40 mg.) distilled gave X, b0.005 50-80° (bath temperature); XI m. 178-80°. N bubbled through 475 mg. VIII and 0.3 g. KOH in 3 cc. O(CH2CH2OH)2, 0.4 cc. N2H4.H2O, and 0.4 cc. absolute EtOH while heating 3 hrs. in an oil bath (160-5°), the condenser removed until the oil bath temperature reached 220°, whereupon refluxing was continued (6 hrs.), the mixture cooled, poured into H2O, extracted with Et2O, the extract washed, dried, fractionated from Et2O, and the residue distilled (10 mm.) gave 286 mg. deoxydihydroeremophilone (XV). Excess O3 passed through 265 mg. XV in 12.5 cc. AcOH at room temperature, the mixture stirred 2 hrs. with 0.5 g. FeSO4 and 35 cc. H2O, poured into H2O, extracted with Et2O, the extract washed with aqueous NaHCO3, dried, and distilled gave 157 mg. 8,9-dimethyl-2-acetyl-cis-decahydronaphthalene (XVI), yellow oil, b0.5-0.6 90-110°, λ (CHCl3), 5.80 μ, R.D. in dioxane [c 0.086 (700-310 mμ), 0.017 (300-285 mμ)]: [α]700 10.3°, [α]589 -5.8°, [α]312.5 -286°, [α]285 211°; 2,4-dinitrophenylhydrazone m. 132-5° (aqueous EtOH). A solution prepared by adding 0.6 cc. (CF3CO)2O to 0.1 cc. 90% H2O2 in 2 cc. CH2Cl2 at 0° added to 126 mg. XVI, the solution stirred 30 min. at room temperature, refluxed 45 min., washed with 5% aqueous Na2CO3, dried, and concentrated; the residue treated with 2 cc. N aqueous NaOH and enough EtOH to yield a homogenous solution, the solution refluxed 3 hrs., an addnl. 2 cc. N NaOH added, heating continued 45 min., the solution poured into H2O, extracted with Et2O, the extracted washed, dried, and evaporated gave 8,9-dimethyl-cis-2-decahydronaphthalenol (XVII). XVII in 5 cc. AcOH oxidized with 0.1 g. CrO3 in 1 cc. H2O and 5 cc. AcOH, kept 1 hr. at room temperature, much H2O added, the product extracted with Et2O, the extract washed, dried, evaporated, and the residue distilled gave 39 mg. 8,9-dimethyl-cis-2-decahydronaphthalenone, oil, b0.5 70-90° (bath temperature), λ 5.80 μ, R.D. in MeOH (c 0.078): [α]700 -20°, [α]589 -29°, [α]315 -178°, [α]307.5 229°. II (1.926 g.), 4.0 g. Bi2O3, and 20 cc. AcOH stirred in an N atmospheric, the temperature slowly raised to 100-5° where it was maintained 1 hr., then cooled, the precipitate filtered off, the filtrate poured on ice with stirring, the product filtered off, washed with H2O, dried, and recrystd. from EtOH gave 800 mg. hydroxyeremophilone (XVIII), m. 64.5-5.0° (MeOH), λ (CHCl3) 2.95, 6.10, and 6.23 μ, λ (EtOH) 309 mμ (log ε 4.01) [shifting to λ 356 mμ (log ε 3.79) on the addition of 1 drop of aqueous KOH], [α]5461 152° (c 2.41, MeOH), identical with natural XVIII. Natural and synthetic XVIII yielded the identical acetate, b0.09

90-100°, m. 67.5-8.0° (MeOH, then pentane), λ (CHCl3) 5.66, 5.99, 6.10, 8.60, 9.80 μ, λ (EtOH) 255 mμ (log ε 4.02), shoulder at 285 mμ (log ε 3.90), R.D. in MeOH [c 0.100 (700-370 mμ), 0.020 (370-317.5 mμ)]: [α]700 92°, [α]589 156°, [α]420-415 336°, [α]387.5 260°, [α]337.5 540°, [α]317.5 -180°.

L4 ANSWER 33 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1959:122408 CAPLUS
DN 53:122408
OREF 53:22060a-f
TI Terpenoids. XL. Absolute configuration of eremophilone
AU Zalkow, Leon H.; Markley, F. X.; Djerassi, Carl
CS Wayne State Univ., Detroit, MI
SO Journal of the American Chemical Society (1959), 81, 2914-15
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 53, 11431b. In order to determine the biogenetic precursor of eremophilone (I) (R = H), hydroxydihydroeremophilone (I, R = OH, cis ring juncture without double bond) (II), and hydroxyeremophilone (III), which do not follow the isoprene rule, it was necessary to ascertain their absolute configuration. (+)-IV treated with MeLi and the product cleaved with acid yielded (+)-trans-2-oxo-4,10-dimethyl-Δ3,6-hexahydronaphthalene (V), m. 42-4°. V hydrogenated over Pd in alkali yielded (+)-trans-4,10-dimethyl derivative (VI) of Δ6-2-octalone, b1.5 110-11°. Wolff-Kishner reduction of VI yielded (+)-trans-1,9-dimethyl derivative (VII) of Δ6-Octalin. VII with (BzO)2 gave the 6α,7α-epoxide which was reduced with LiAlH4 to the alc. The alc. was oxidized to (+)-trans-5,10-dimethyl derivative (VIII) of 2-octalone, m. 29-30°. VIII with (CO2Et)2 and NaH gave the glyoxalate, which was decarbonylated in the presence of powdered glass to (+)-trans-3-ethoxycarbonyl-5,10-dimethyl derivative (IX) of 2-decalone, b0.01 65°. IX was converted to the cycloethylene ketal which with MeMgI followed by dehydration of the carbinol, m. 55-60° with POCl3 in pyridine yielded (+)-trans-2-ethylenedioxy-3-isopropenyl-5,10-dimethyl derivative (X) of Decalin, b0.1 90-105°. Hydrogenation of X yielded (+)-trans-2-ethylenedioxy-3-isopropenyl-5,10-dimethyl derivative of Decalin, which with HCl-MeOH gave trans-3-isopropyl-5,10-dimethyl derivative (XI) of 2-decal one, b0.04 75-85°, pos. rotatory-dispersion Cotton effect with peak at [α]3120 530° (c 0.21, MeOH); 2,4-dinitrophenylhydrazone m. 169-72°. The Me ether of III hydrogenated over Pd in EtOH, the tetrahydro derivative equilibrated with alkali, and the product demethoxylated with Ca in liquid NH3 yielded XI, identical in all respects with XI prepared above. These interconversions demonstrated that I and its relatives possessed the absolute configurations implicit in stereoformulas I, II, and III and that the eudalenoid biogenetic precursor had the same absolute configuration as eudesmol.

L4 ANSWER 34 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1957:25606 CAPLUS
DN 51:25606
OREF 51:5110a-i,5111a-b
TI Optical rotatory dispersion studies. VII. Application to problems of absolute configuration
AU Djerassi, Carl; Riniker, Rosemarie; Riniker, Bernhard
CS Wayne State Univ., Detroit, MI
SO Journal of the American Chemical Society (1956), 78, 6362-77
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
OS CASREACT 51:25606

AB cf. C.A. 51, 1220i. The rotatory dispersion curves of saturated and unsatd. steroid ketones have been studied and their characteristic features found to be a reflection of the appropriate bicyclic nucleus; this permits an enormous extension of the rotatory dispersion method to many other alicyclic ketones and absolute configurations can be assigned on the basis of coincidence of rotatory dispersion curves with those of known reference compds. trans-9-Methyl-1-oxo-Δ2,6-hexahydronaphthalene (4.75 g.) in 50 cc. MeOH hydrogenated 40 min. over 200 mg. 10% Pd-C, filtered, and evaporated, and the residue chromatographed on 30 g. Al2O3 yielded (+)-trans-9-methyl-1-decalone (I), b10 120° (bath); 2,4-dinitrophenylhydrazone, orange needles, m. 159-60° (from MeOH-CH2Cl2). I (1.0 g.) added to 2.6 g. dry NaOMe, 60 cc. dry C6H6, and 4.5 cc. HCO2Et, the mixture stirred overnight at 30°, and the base-soluble product (1.15 g.) distilled gave 850 mg. (-)-trans-9-methyl-2-hydroxymethylene-1-decalone (II), pale yellowish oil, b12 150° (bath), [α]D -16.5° (MeOH); it gave a dark purple color with FeCl3 in MeOH. II in MeOH treated with excess 2,4-(O2N)2C6H3NHNH2 in the presence of HCl gave initially a dark red product which changed on warming to the pyrazole derivative, yellow leaflets, m. 228-9°. II (305 mg.) in 25 cc. (CH2Cl)2 ozonized at -70° during about 4 min. and evaporated, the residue boiled with 10 cc. H2O 0.5 hr., and the product isolated with Et2O yielded 210 mg. (+)-trans-9-methyldecalin-1,2-dione (III), yellowish oil, b0.02 90°; it gave a dirty violet color with FeCl3. III (270 mg.) in 60 cc. 5% KOH in MeOH treated during 45 min. with 15 cc. 30% H2O2 at reflux and processed in the usual manner yielded 180 mg. (-)-trans-1-methyl-1-carboxycyclohexane-2-acetic acid (IV), m. 137-8° (from Me2CO-hexane). IV (300 mg.) and 16 mg. Ba(OH)2 heated at 300-30° and the distillate (160 mg.) chromatographed on 10 g. Al2O3 gave (-)-trans-8-methylhydrindan-1-one (V), b10 90-5°; 2,4-dinitrophenylhydrazone, orange leaflets, m. 162-2.5°. (+)-trans-1-Methylcyclohexane-1,2-diacetic acid (40 mg.) pyrolyzed with 3 mg. Ba(OH)2 gave 25 mg. 2-oxo isomer (VI) of V, b10 95°; 2,4-dinitrophenylhydrazone, m. 157-61° (from CH2Cl2-MeOH). Eremophilone (VII) (600 mg.) in 40 cc. MeOH hydrogenated at ambient conditions over 200 mg. 10% Pd-C gave 560 mg. cis-tetrahydroeremophilone (VIII), b10 160° (bath); 2,4-dinitrophenylhydrazone, yellowish orange needles, m. 148-50° (from CH2Cl2-MeOH). VIII (400 mg.) heated 0.5 hr. with 5 cc. 2N HCl and 5 cc. MeOH gave the trans isomer (IX) of VIII, b10 160° (bath); 2,4-dinitrophenylhydrazone (X), m. 179-80°. VII reduced with Na in EtOH and oxidized with CrO3 in AcOH gave trans-dihydroeremophilone (XI). IX (150 mg.) heated overnight at 210° with 150 mg. Na and 0.15 cc. N2H4 and the neutral product chromatographed on 5 g. Al2O3 yielded 120 mg. trans-deoxytetrahydroeremophilone (XII), b10 130° (bath). XI (130 mg.) yielded similarly 98 mg. trans-deoxydihydroeremophilone (XIII); it gave a yellowish brown color with C(NO2)4. 5-Cholesten-4-one (XIV) (350 mg.), m. 110-12°, in 50 cc. Et2O hydrogenated 5 min. over 200 mg. 10% Pd-C yielded 150 mg. coprostan-4-one (XV), m. 111-12° (from MeOH-Et2O), and 120 mg. impure cholestan-4-one (XVI), m. 77-95°; the crude XVI heated 10 min. on the steam bath with 5 cc. MeOH and 0.2 cc. concentrated HCl gave XVI, m. 95-100°. Pure XV (20 mg.) heated 15 min. with 5 cc. 5% KOH in MeOH, diluted with H2O, and filtered gave pure XVI, m. 99-100° (from CH2Cl2-MeOH). The rotatory dispersion values are given for compds. I through VII, X through XV, (+)-cis-8-methylhydrindan-5-one, Me 2-oxo-A-norcholanate, 3-oxo-A-norcholanic acid, androstan-17-one, 14β-androstan-3β-ol-17-one acetate, 14β,-22a,25a,5α-spirostan-2α,3β-diol-15-one, androstan-3β-ol-16-one, 5-pregnene-3,16,20-trione 3,20-bis(ethylene ketal), 2-oxo-A-norcholestane, 3-hydroxy-16-oxo-1,3,5-estratriene, 19-nortestosterone, 8,13-dimethyl-8-methoxycarbonyl-2-oxo-Δ1(11)-dodecahydrophenanthrene, 4-methyl-4-cholesten-3-one, 4-cholesten-3-one, α- and β-cyperone, (+)-epi-α-cyperone,

(+)-dihydroepi-α-cyperone, carissone,
(-)-1,14-dimethyl-2-oxo-Δ)1(11),6-decahydrophenanthrene,
(-)-3-oxo-eusanton-4-enic acid, (-)-santonin, 1,4-cholestadien-3-one,
α-,β-, and γ-tetrahydrosantonin, 17aα- and
17aβ-methyl-D-homoandrostan-3β-ol-17-one, friedelin,
(-)-1,14-dimethyl-2-oxo-Δ1(11),6,9-octahydrophenanthrene,
4,6-cholestadien-3-one, the norketone from phyllocladene,
epoxynorcafestanone, the ketone from cafestol, the alc. from cafestol,
steviol, isosteviol, garryfoline, cuauchichicine, F-dihydrogarryfoline,
F-dihydrocuauchichicine, yohimbone, yohimbane,
(+)-cis-13-methyl-3,4-dimethoxy-5,6,7,8,9,10,13,14-octahydrophenanthrene
and 6-oxo derivative, 4-cholesten-6-one, ψ-santonin,
1-oxo-7-hydroxy-Δ5(10)-santenic acid, 1-oxo-7-hydroxysantanic acid,
and (-)-trans-1,1,3-trimethyl-3-carboxycyclohexane-2-acetic acid.

L4 ANSWER 35 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1954:60381 CAPLUS
DN 48:60381
OREF 48:10700e-i,10701a-b
TI On the structure of eremophilone
AU Geissman, T. A.
CS Univ. of California, Los Angeles
SO Journal of the American Chemical Society (1953), 75, 4008-11
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB A reexamn. of the oxidation of hydroxyeremophilone (I) has disclosed that the product of the oxidation, formerly regarded as having the composition C12H1803 (cf. Bradfield, et al., C.A. 32, 5816.9), is really a compound C16H2204 having structure (II), which was derived from the ultraviolet absorption spectrum. I, prepared by the saponification of the purified benzoate (10.1 g.), in 60 cc. glacial AcOH treated with stirring dropwise during several hrs. with 7 g. CrO3 in 50 cc. 80% AcOH, the excess CrO3 destroyed with NaHSO3, the solution poured into H2O, the AcOH removed by steam distillation, the oily residue taken up in Et2O, the solution extracted with six 2-cc. portions of N NaOH, and the extract saturated with CO2 precipitated 0.9 g. greenish yellow crystals, which on recrystn. from aqueous MeOH gave II colorless prisms, m. 192.5-3.5°; λmaximum 238 mμ (log ε 3.88) in EtOH, 277 (3.93) in alkali. II (50 mg.) in 1 cc. Ac2O and 0.5 cc. dry pyridine heated to boiling, the solution let stand overnight, the excess Ac2O decomposed with ice, and the resulting crystalline material, recrystd. from MeOH gave the acetate (III), tiny, colorless, stout needles, m. 163-4°, showing end absorption rising to a plateau at about 215 mμ (4.07). Equal wts. of II, NH2OH.HCl, and NaOAc in 50% aqueous EtOH refluxed 1 hr., and the mixture diluted with H2O and cooled in ice gave the oxime of II, tiny, colorless prisms, m. 192-3°, λmaximum 239 mμ. The structure II advanced for the oxidation product of I offers addnl. support for the unnatural structure (IV) proposed for I. The ultraviolet absorption spectra of II, 1.15 + 10-4M in EtOH and 1.15 + 10-4M in 0.1N KOH-EtOH, and of III, 1.10 + 10-4M in EtOH and 1.10 + 10-4M in EtOH, are recorded. (In the original, the numbers under figures IV and VI are interchanged.)

L4 ANSWER 36 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1954:60380 CAPLUS
DN 48:60380
OREF 48:10698e-i,10699a-i,10700a-e
TI Podophyllotoxin studies. Reductive methods in the synthesis of Tetralin lactones from 1-tetralone derivatives

AU Walker, Gordon N.
CS Natl. Inst. of Health, Bethesda, MD
SO Journal of the American Chemical Society (1953), 75, 3393-7
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
AB cf. preceding abstract To 1.4 g. 3-carbethoxy-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydro-1(2H)naphthalenone (I) in 50 cc. MeOH was added 0.45 g. NaBH4, the solution refluxed 0.5 h., most of the EtOH evaporated, the residue treated with H2O, the product extracted with EtOAc, the extract washed with H2O, evaporated, the residue (showing an IR band at 2.85-3.0 μ) refluxed 2.5 h. with 10 g. NaOH in 50 cc. H2O, the resulting solution cooled, diluted to 125 cc., filtered, acidified strongly with HCl, chilled several days, the crystals extracted with EtOAc, and the extract washed with several portions each of aqueous NaHCO3 and H2O, dried with MgSO4, and evaporated, leaving a discolored residue (0.25 g., 20%), which crystallized readily from MeOH to give 1-hydroxy-3-carboxy-4-(3, 4-dimethoxyphenyl)-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene lactone (II), colorless crystals, m. 180.5-1.5° (all m. ps. are corrected), λCHCl3max. 5.65 μ, λEtOHmax. 283 mμ. 3-Carboxy-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydro-1(2H)naphthalenone (0.9 g.) in 100 cc. glacial AcOH hydrogenated 2 h. at 40 lb. pressure and 80° over 0.8 g. 5% Pd-on-C, the solution filtered, the AcOH evaporated, the residue dissolved in EtOAc, the solution washed with aqueous NaHCO3 and H2O, dried, evaporated, and the residue (0.05 g., 6%) recrystd. from MeOH gave II, m. 179-81°; the NaHCO3 washings acidified gave 0.5 g. crystals which m. 180-90° after several recrystns. from EtOAc. To NaOMe prepared from 12.0 g. Na and dried 15 min. in vacuo at 100° was added 54.5 g. I suspended in 170 g. HCO2Et and 800 cc. dry Et2O, the mixture swirled several hrs., let stand overnight, diluted with an equal volume of cold H2O, shaken thoroughly, the organic layer washed with 5% aqueous NaOH, the combined alkaline solution acidified with HCl, chilled, and the product washed several times with H2O, pressed dry, and triturated with a small quantity MeOH to yield 54.9 g. (94%) 2-hydroxymethylene-3-carbethoxy-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydro-1(2H)-naphthalenone (III), nearly colorless crystals, m. 166-70°; repeated recrystn. from MeOH, C6H6, or EtOH gave crystals with a yellow cast, m. 174-7.5°, λCHCl3max. 5.76 and 6.08 μ, soluble in 5% aqueous NaOH, insol. in aqueous NaHCO3, giving a deep red color with FeCl3 with 2,4-(O2N)2C6H3NHNH2 (IV) a dark red gummy precipitate which became crystalline on standing in EtOH and yielded on recrystn. from EtOH-EtOAc a derivative, red-orange crystals, m. 236-7.5°, the anal. of which did not agree with any of several possible formulas. III (3.4 g.) in 100 cc. 5% aqueous NaOH warmed 15 min. on a steam cone, acidified with HCl, the initially formed gum cooled to room temperature, and the resulting crystalline solid washed with several portions of cold H2O and air-dried gave 3.1 g. crude 2-hydroxymethylene-3-carboxy-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydro-1(2H)-naphthalenone (V), yielding in contact with MeOH, Et2O, or C6H6 an oily material, soluble in aqueous NaHCO3, and giving a deep greenish brown color with FeCl3, λCHCl3max. 3.00 (broad), 5.85, 6.09, 6.00 μ (very weak). III (1.5 g.) and 2.1 g. LiAlH4 in 500 cc. dry Et2O and 100 cc. dry C6H6 stirred 3 wk at room temperature, then 0.5 h. with 40 cc. H2O and 30 cc. 50% H2SO4, the Et2O solution washed with 2 small portions of 5% aqueous NaOH and small portions of dilute AcOH, aqueous NaHCO3, and H2O, dried, evaporated, and the residual 0.6 g. gum taken up in Me2CO, the solution evaporated slowly, and the residual crystals washed with MeOH and recrystd. from MeOH

gave 0.3 g. (23%) 2-methyl-3-hydroxymethyl-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydro-1(2H)-naphthalenone, colorless crystals, m. 168.5-70°, λCHCl3max. 2.90. 5.98 μ, giving a red precipitate with IV. III (1.1 g.) in 100 cc. glacial AcOH containing 1.0 g. 5% Pd-on-C shaken 2 h. at 40 lb. and 80° under H, the mixture filtered, the filtrate evaporated, and the oily residue (1.1 g.) let stand in MeOH-EtOH and recrystd. from MeOH gave 1-(3,4-dimethoxyphenyl)-2-carbethoxy-3-methyl-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (VI), colorless crystals, m. 141-3°, λCHCl3max. 5.80 μ, insol. in alkali, and did not give a FeCl3 reaction. When the preparation of VI was carried out at room temperature, a product, m. 134-6.5°, was obtained which had in CHCl3 an IR spectrum nearly identical with that of VI. VI (1.0 g.) refluxed 2 h. with 5 g. NaOH in 15 cc. H2O and 5 cc. EtOH, the solution diluted with 150 cc. H2O, filtered, acidified with HCl, chilled overnight, and the crystalline deposit washed with H2O, pressed dry, and recrystd. from MeOH yielded 0.8 g. 1-(3,4-dimethoxyphenyl)-2-carboxy-3-methyl-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (VII), colorless crystals with 0.5 mol EtOH, m. 224.5-27° with shrinking, λCHCl3max. 5.84 μ, soluble in aqueous NaHCO3. V (3.1 g.), in 100 cc. glacial AcOH hydrogenated 3 h. at 40 lb. pressure and 80° over 3 g. 5% Pd-on-C, the hot solution filtered, the filtrate again hydrogenated under the same conditions over 3 g. fresh catalyst, filtered again, evaporated, the residue partitioned between EtOAc and H2O, the EtOAc solution washed with H2O, extracted with 2 portions aqueous NaOH, the aqueous extract acidified with HCl, chilled, and the crystalline deposit washed with H2O, air-dried, and recrystd. from MeOH gave 0.7 g. (24%) VII, colorless crystals, m. 233-6° with shrinking and browning, soluble in aqueous NaHCO3, λCHCl3max. 5.84 μ; in some runs there was formed an unidentified, extremely difficultly soluble, colorless solid, which was soluble in H2O and did not melt below 350°. III (1.25 g.), 1.1 g. (CH2OH)2, and 0.22 g. p-MeC6H4SO3H in 25 cc. dry PhMe refluxed 3 h. with azeotropic removal of the H2O, addnl. (CH2OH)2 added after 1 h., the solution cooled, diluted with 10 vols. EtOAc, washed with 5% aqueous NaOH, dilute AcOH, aqueous NaHCO3, and H2O, dried with MgSO4, evaporated, and the residual viscous oil triturated with MeOH gave 0.7 g. (51%) ethylene ketal (VIII) of III, colorless crystals, m. 165-7.5°; recrystd., it m. 167.5-8.5° λCHCl3max. 5.76, 5.98, very slowly gave with IV a red precipitate VIII (0.7 g.) in 50 cc. MeOH treated with 0.20 g. NaBH4, the solution refluxed 0.5 h., evaporated to dryness, the residue shaken with H2O and EtOAc, and the EtOAc solution washed with several portions of H2O, dried with MgSO4, and evaporated gave 0.7 g. crude 1-hydroxy-2-ethylenedioxymethyl-3-carbethoxy-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (IX), glass, λCHCl3max. 2.86, 5.77 μ. Crude IX (0.7 g.) in 75 cc. H2O and 25 cc. EtOH and 5 cc. concentrated HCl warmed 1 h. on the steam cone, the MeOH evaporated, the residue extracted with EtOAc, and the extract washed with several portions aqueous NaHCO3 and H2O, dried, and evaporated gave an oily product, λCHCl3max. 5.77, 5.96, 6.11 μ, darkened slowly in air, gave rapidly with IV a 2,4-dinitrophenylhydrazone, red crystals, C30H30N4O10, m. 234-7° (triturated with EtOH, from dry C6H6). III (4.0 g.) in 80 cc. H2O and 40 cc. MeOH treated with 8.0 g. NaBH4 in several portions, the mixture refluxed 3 h., acidified, most of the MeOH distilled off, the residual solution diluted with 150 cc. H2O, filtered, the filtrate chilled in ice, gradually acidified with 20 cc. concentrated HCl in 40 cc. cold H2O, the voluminous precipitate washed with two 25-cc. portions of cold H2O, pressed dry, dissolved immediately in 50 cc. MeOH, the solution diluted with 300 cc. Et2O, stirred until the crystallization was complete, and the crystalline solid air-dried gave 1.0 (26%) 2-hydroxymethyl-3-carboxy-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-1,2,3,4-tetrahydro-1-naphthol (X), m. 178-88°, crystallizing from MeOH in fluffy crystals, m. 217-17.5° with shrinking (decomposition), λCHCl3max. 2.80, 5.91 μ, soluble in aqueous

NaHCO3. X (0.7 g.) in 90 cc. glacial AcOH refluxed 2.5 h., most of the AcOH distilled off, the residue dissolved in a small amount of MeOH, the solution refrigerated overnight, and the crystals (0.4 g.) recrystd. from MeOH gave 1-(3,4-dimethoxyphenyl)-2-carboxy-3-hydroxymethyl-6,7-dimethoxy-1,4-dihydronaphthalene lactone, colorless dense crystals, m. 213-15°, λCHCl3max. 5.68 μ, λEtOHmax. 284 mμ. X (0.5 g.), 1.0 g. 5% Pd-on-C, and 100 cc. glacial AcOH shaken 2 h. under H at 40 lb. pressure and 80°, the mixture filtered, the solution evaporated to dryness, the residue dissolved in EtOAc, the solution washed with 2 portions of 5% aqueous NaOH, dilute AcOH, aqueous NaHCO3, and H2O, dried, evaporated, and the residue (0.4 g.) crystallized from MeOH gave 1-(3,4-dimethoxyphenyl)-2-carboxy-3-hydroxymethyl-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene lactone (XI), colorless crystals, m. 189-90.5° with softening; λCHCl3max. 5.60 μ, λEtOHmax. 283 mμ. XI heated 2 h. at 100° in 30% NaOH, the resulting sparingly soluble salt dissolved by diluting the mixture with H2O, the solution filtered, acidified strongly with HCl, let stand in ice overnight, and the crystalline deposit washed with H2O and recrystd. from MeOH gave XI, m. 187-91°. X (0.7 g.) heated 0.5 h. at 150° the resulting solid (insol. in aqueous NaHCO3) taken up in 50 cc. Ac2O, the mixture refluxed 3 h., the solution evaporated to dryness, and the crystalline residue recrystd. several times from MeOH gave 1-acetoxy-2-hydroxymethyl-3-carboxy-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene lactone, m. 211-13°, colorless needles, λCHCl3max. 5.58, 5.74 μ, λEtOHmax. 282 mμ. The complete IR spectra of the compds. prepared are recorded in Document 3858 from the American Documentation Inst., Library of Congress, Washington 25, D.C.

L4 ANSWER 37 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1941:25282 CAPLUS
DN 35:25282
OREF 35:4005h-i,4006a-i,4007a-e
TI Constitutions of eremophilone, hydroxyeremophilone and hydroxydihydroeremophilone. IV
AU Gillam, A. E.; Lynas-Gray, J. I.; Penfold, A. R.; Simonsen, J. L.
SO Journal of the Chemical Society (1941) 60-8
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C. A. 33, 2512.2. Corrected formulas are given for hydroxyeremophilone (I, R = H) and its dihydro derivative (cf. part III). Many of the reactions of I suggest that it is a potential 1,2-diketone, with one of the CO groups in position 5. The Me ether of I (R = Me) on reduction in EtOH with Pd-norite gives an impure dihydro derivative (II), b16 168°, d19.819.8 1.4848, [α]5461 17.2° (2,4-dinitrophenylhydrazone, yellow, m. 140°); reaction of II with MeMgI gives an oil (b16 148-60°), which, heated with Se at 270° for 12 h. and at 300-20° for 36 h., gives 1,6,7-Me2C10H5CHMe2; if no mol. rearrangement occurs during the dehydrogenation the structure of the ether is I (R = Me). Eremophilone (III) (10 g.) is reduced by (iso-PrO)3Al in iso-PrOH to 7.5 g. of eremophilol (IV), b13 164-5°, nD 1.5202, [α]5461 - 55.6° (MeOH, c 5.25); 3,5-dinitrobenzoate, m. 88-9°, [α]5461 - 149.4° (AcOEt, c 0.813); the absorption spectra exhibit maximum at 2440 and 2750 A. (ε 193 and 188), which rules out the possibility of the presence of 2 conjugated ethylenic linkages in IV and therefore in III (the 2 bands are almost certainly due to traces of impurities). The action of O3 on III gives a keto acid, probably HO2CCH2CHAcCH2CMe(CO2H)CHMeCH2CH2CO2H, whose Me ester b18 220°;

further oxidation with alkaline NaOBr gives CHBr3 and the acid HO2CCH2CH-(CO2H)CH2CMe(CO2H)CHMeCH2CH2CO2H (a gum), which forms a tri-Ag salt, and a tetra-Me ester, b5 203-5°, [α]5461 - 17.5° (MeOH, c 6.03). This confirms the structure of III proposed in part III. Contrary to the results in C. A. 27, 497, III yields a crystalline tetra-Br derivative, iridescent prisms, decomps. 116°; it is unstable and decomps. on warming the EtOH or AcOEt solution The yellow color of molten I (R = H) and of its solns. suggests that it can exist also as a 1,2-diketone. During the discussion of the question of the structure the effect of the ethylenic linkage being cyclic or exocyclic on the absorption due to the α,β-unsatd. ketone was studied in piperitone (V) and pulegone (VI); whereas the low-intensity absorption band due to the CO group is unaltered in the 2 cases, the high-intensity band due to the conjugated system is displaced from 2355 A. in V to 2520 A. in VI, the change presumably being due to the difference in the ethylenic linkage. In diosphenol (VII) (which is identical with V except for the presence of a HO group) there is a displacement of the ethylene band from 2355 to 2740 A. and the disappearance or masking of the band due to the CO group. The location to be expected for I (R. = H) would be similar to that of VII-2740 A.; actually the main maximum is at 3125 A. with a subsidiary at 2775 A. To explain this location necessitates a formula containing a longer chain of ethylene linkages and the most probable way to obtain this is to postulate a tautomerism of I to VIII in EtOH solution This was tested by examining the Bz derivative (I, R = Bz) in which the tautomeric change could not occur; after allowing for the absorption of the Bz radical, the absorption of I (R = H) in the combined state is quite different from that of the free compound and the displacement to longer wavelengths in the case of the free compds. is consistent with the postulated tautomeric form. The absorption curves for III oxide and dihydroeremophilone oxide are given; the difference in absorption between III and its oxide is sufficient to indicate that the O atom in the oxide has attached itself to the ethylene linkage originally in conjugation with the CO group.

L4 ANSWER 38 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1940:33494 CAPLUS
DN 34:33494
OREF 34:5058f-i,5059a-c
TI Experiments on the synthesis of 1,2-dimethylcyclohexaneacetic acid
AU Copp, F. C.; Simonsen, J. L.
SO Journal of the Chemical Society (1940) 415-18
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable
AB The acid (I) C10H18O2 obtained by the reduction of the keto acid resulting from the ozonolysis of hydroxyeremophilone benzoate (C. A. 33, 2512.2) is not identical with d-2,2-dimethylcyclohexaneacetic acid (C. A. 32, 5794.7); therefore, the synthesis of the 1,2-isomer was undertaken. Et 4-keto-2,3-dimethyl-2-cyclohexene-1-carboxylate (10 g.), refluxed with 5 g. KOH in 30 cc. EtOH for 12 h., saturated with CO2 and distilled with steam, gives 5.6 g. of 2,3-dimethyl-2-cyclohexen-1-one, b15 91°; catalytic reduction yields 2,3-dimethylcyclohexanone (IA), b13 69-70°, b769 181-2°. IA (10 g.) was transformed into the Na derivative (refluxing with 3.1 g. NaNH2 in C6H6 in a N atmospheric for 6 h.), the solution cooled in ice and condensed with 12.5 g. BrCH2CO2Et (1 h. at 0° and 2 h. at the boiling temperature); the mixed product was transformed into the Na derivative and condensed with (CO2Et)2; the mixture was poured on ice, the oil removed with ether and the aqueous alkaline solution acidified; the oil which separated was dissolved in ether, dried and distilled at 160-80°/16 mm.; hydrolysis with dilute H2SO4 gives a viscous oil which yields an α-semicarbazone, m. 197-8° and a more readily soluble (in MeOH) β-isomer, decomps.

192°; 6-keto-1,2-dimethylcyclohexaneacetic acid, m. 107°. The yield was too small to continue the experiment The portion which did not react with (CO2Et)2 was Et 2-keto-3,4-dimethylcyclohexaneacetate, b16 144°. Condensation of the Na derivative of 2-methylcyclohexanone and BrCH2CO2Et (heating 5 h. in Et2O) gives, after treatment with (CO2Et)2 as above, Et 6-keto-5-carbethoxy-2-methylcyclohexaneacetate, b20 170-90°; 2-keto-1-methylcyclohexaneacetic acid, m. 77-8°; Et ester (II), b19 142°; semicarbazone, decomps. 182°. The Et ester and iso-Am formate with Na in ether give the hydroxymethylene derivative, whose semicarbazone m. 151°; anal. indicates that the iso-Am ester had been formed. II and MeMgI, followed by hydrolysis of the ester, give the lactone of 6-hydroxy-1,2-dimethylcyclohexaneacetic acid (III), which could not be purified but from which the keto acid was removed with H2NCONHNH2; III m. 73°. No satisfactory method could be found for the reduction of III; Clemmensen reduction yields a very small amount of dl-1,2-dimethylcyclohexaneacetic acid, b16 153°; p-phenylphenacyl ester, m. 61-2°; cinchonidine salt, m. 141-2°, [α]5461 -95° (CHCl3, c 1.06); the regenerated acid yields a p-phenylphenacyl ester, m. 65-7°, [α]5461 -6°(AcOEt, c 4); the acid recovered from the above salt yields a p-phenylphenacyl ester, m. 62-5°, [α]5461 8° (AcOEt, c 3.64). Mixed m. ps. show that I is d-1,2-dimethylcyclohexaneacetic acid. Therefore, the Me groups in eremophilone and hydroxyeremophilone occupy the 1,10-positions and these ketones are not isoprene derivs.

L4 ANSWER 39 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1939:17146 CAPLUS
DN 33:17146
OREF 33:2512b-f
TI Constitution of eremophilone, hydroxyeremophilone and hydroxydihydroeremophilone. III
AU Penfold, A. R.; Simonsen, J. L.
SO Journal of the Chemical Society (1939) 87-9
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C. A. 32, 5816.9. It has been suggested to the authors by R. Robinson that eremophilone is probably represented by I; hydroxyeremophilone would then be II and hydroxydihydroeremophilone would be III. If II is correct, then the keto acid, C10H16O3, obtained by ozonolysis of its benzoate would be IV, yielding on Clemmensen reduction the cyclohexyl acid V. The Me ester of V, b19 110-12°, on dehydrogenation with Se gives o-xylene; this fact supports the structure for II. Reduction of II with Na in EtOH gives a 1,3-glycol(?) which with Pb(OAc)4 in AcOH yields the dibasic acid, C15H26O4, previously obtained from II and III; this oxidation must proceed abnormally, for the Criegee reagent is generally assumed to be diagnostic for 1,2-glycols. The proposed representation of II is not in accord with the so-called "isoprene rule" and if correct, the implications are far-reaching. A rigid proof must await the synthesis and resolution of the 2 possible dl-modifications of IV.

L4 ANSWER 40 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1938:41795 CAPLUS
DN 32:41795
OREF 32:5816i,5817a-g
TI Constitution of eremophilone, hydroxyeremophilone and hydroxydihydroeremophilone
AU Bradfield, A. E.; Hellstrom, N.; Penfold, A. R.; Simonsen, J. L.
SO Journal of the Chemical Society (1938) 767-74
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable

AB cf. C. A. 30, 5205.3; 31, 5345.3. The observation that tetrahydroeremophilone after treatment with MeMgI and Se dehydrogenation gave 1,5,7-Me2(iso-Pr)C10H5 and not the 1,3,7-isomer showed that the structure proposed by Bradfield, Penfold and Simonsen (C. A. 27, 497) could not correctly represent eremophilone (I) (from the wood of Eremophila mitchelli). The CO group in I is in position 5 and not 3 as previously assumed. A more convenient method for the separation of I and hydroxyeremophilone (II) is given and evidence is presented for the occurrence in the oil of a 4th ketone, C15H22O, whose 2,4-diphenylhydrazone, yellow, m. 155-6.5°. The assumption as to the location of the CO group in I is supported by the conversion of hydroxymethyleneeremophilone into 1,6,7-Me2(iso-Pr)C10H5 on reduction and Se dehydrogenation. Attempts to establish the presence of a CO group in II or its esters were unsuccessful. II yields a Me ether (III), b13 180°; this is not reduced by (iso-PrO)3Al; it gives no color with FeCl3; Na in iso-AmO2CH-Et2O forms an oil, which gives a deep red color with FeCl3 and reacts with CO reagents, yielding amorphous derivs. The benzoate (IV) of II, catalytically reduced and the resulting gum hydrolyzed, yields β-hydroxydihydroeremophilone (V), b13 169-72°, m. 89-90°, [α]5461 42° (MeOH c 2.07); it gives an intense green color, changing to blue, with FeCl3. The oil from which V crystallizes on treatment with NaOH and H2O2 in MeOH at 50°, gives a phenol, C15H24O3, m. 136-7° (olive-green color with FeCl3) and an acid, C15H24O4, m. 193-5°, which is stable to KMnO4 in alkali and gives a liquid anhydride with AcCl. Oxidation of II with CrO3 in dilute AcOH gives a phenol, C12H18O3, m. 193-4.5°; Ac derivative, m. 164-5°; Me ether, m. 121-2°; and a keto acid, C10H16O3 (VI), m. 105-7°; semicarbazone, decomps. 207-8°. II and III give the same phenol and acid. When IV in CCl4 is ozonized at 0° until O3 is present in the issuing gases, there results an oxide, C19H20O5, m. 186-8°; hydrolysis gives VI; there is also formed a small amount of a gum which gives a semicarbazone, m. 166° (not identified). With excess of O3 II yields VI and a moloxide of BzOH, C7H6O4, decomps. 230-2°. Reduction of VI gives a liquid acid, C10H18O2, whose p-phenylphenacyl ester, m. 65-70°, [α]5461 15.3° (AcOEt, c 1.026); this is not 2,2-dimethylcyclohexylacetic acid. Various structures are discussed for I and its derivs. and at present it is believed that I and II must contain the skeletons VII and VIII, resp.

L4 ANSWER 41 OF 42 CAPLUS COPYRIGHT 2009 ACS on STN
AN 1936:39249 CAPLUS
DN 30:39249
OREF 30:5205b-i,5206a-f
TI α-Cyperone, a sesquiterpene ketone from the oil of Cyperus rotundus
AU Bradfield, A. E.; Hedge, B. H.; Rao, B. Sanjiva; Simonsen, J. L.; Gillam, A. E.
SO Journal of the Chemical Society (1936) 667-77
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB The crude essential oil of Cyperus rotundus (ketone content 35-54%) yielded the semicarbazone of I, m. 216°, [α]5461 178° (CHCl3, c 5), and a liquid isomer, which, on hydrolysis, gave a ketone, C15H22O, b5 145-6°, d3030 0.9879, nD25 1.5138, [α] 28.5°. α-Cyperone (I), b20 177°, d2525 0.9946, nD30 1.5283, [α]5461 138°, [α]5780 118.6°; oxime, m. 150.5°, [α]5461 134° (EtOH, c 1.35); 2,4-dinitrophenylhydrazone, red with bronze reflex, m. 209-10°, nitroguanylhydrazone, decomposing 203-4°, [α]D 196° (CHCl3, c 2.5); oxidation with percamphoric acid is slow, 1.2 atoms of O being absorbed per mol. after 24 hrs. and 1.7 after 8 days. HCO2Am and Na react with I in Et2O in 12 hrs., giving the hydroxymethylene derivative, brown

oil (deep reddish violet color with alc. FeCl3);
2,4-dinitrophenylhydrazone, dark brown, m. 159-60°. Catalytic
reduction (Pd) of I gives a tetrahydro derivative (II), b14 151-2°,
d2525 0.9597, nD25 1.4871, [α]5461 14.8°, [α]5780
12.4°; semicarbazone, decomposing 173-5°; oxime, m.
116-17.5°; 2,4-dinitrophenylhydrazone, orange, m. 151-2°;
hydroxymethylene derivative (IIA), oil, giving a purple-red color with FeCl3
(2,4-dinitrophenylhydrazone, red with Cu sheen, m. 182-3°).
Reduction of I with Na and EtOH gives dihydro-α-cyperol (III), b15
167-8°, nD25 1.5121, [α]5461 17.7° (EtOH, c 2.26);
3,5-dinitrobenzoate (IV), m. 157-8°. Dehydrogenation with Se at
200° and then 250° for 40 hrs. gives eudalene. Oxidation of
I with O3 gives a liquid di-basic keto acid (V), whose di-Me ester, b11
190-7°, was characterized as the semicarbazone, decomposing
245-6°; HCHO is also formed. Alkaline H2O2 and I give β-cyperone
and an acid, probably 6-acetyl-1-methyl-4-isopropenylcyclohexane-1-
carboxylic acid (VA), from the enolic form of I, m. 112°,
[α]5461 62.6° (MeOH, c 2.22); semicarbazone, decomposing
180-1°; phenylsemicarbazone, decomposing 200°. The action of
O3 on the semicarbazone of I gives a semicarbazone, C15H23O4N3, m.
185-7°, which is a powerful reducing agent; its formation provides
proof that only 1 of the CH:CH linkages in I is exocyclic. III with O3
gives HCHO and a ketonic alc., further oxidized by CrO3 to the diketone
(VI), C14H22O2, whose dioxime decomposes 258-9° and disemicarbazone
decomposes 251-2°; in 1 experiment with impure III, an alc. was formed,
isolated as a di- or tri-phenylsemicarbazone, m. 222-3°. With O3
IV gives a ketone, C21H26O7N2, m. 148-9°, from which CHI3 was
obtained on oxidation with Fuson's reagent; since VI did not give CHI3, it
was necessary to establish directly the position of the CO group, which
was effected by treating II with MeMgI and dehydrogenating the alc. with
Se, whereby 1,2-dimethyl-7-isopropylnaphthalene (VII) was formed; this
proves that II is 1,10-dimethyl-7-isopropyldecal-2-one. Reduction and
dehydrogenation of IIA gives the hydrocarbon C15H18, whose picrate,
orange, m. 102.5-4°, and sym-trinitrobenzene derivative, bright yellow,
m. 116-18°; this is not identical with any known C10H8 compound
Heating the semicarbazone of I with EtONa at 200° for 6-7 hrs.
gives α-cyperene, C15H24, b15 132-3°; O3 gives HCHO but no
Me2CO; it could not be reduced by Na and EtOH or AmOH. I is isomerized by
aqueous (CO2H)2 or MeOH-KOH to β-cyperone, b16 175-6°, d2525
0.9945, nD20 1.5414, [α]5161 239°; semicarbazone, decomposing
207°; oxime, m. 138°, [α]5461 217° (EtOH, c
1.45); 2,4-dinitrophenylhydrazone, red with metallic reflex, decomposing
218-19°; nitroguanylhydrazone, m. 197°, [α]D
220° (CHCl3, c 2.5); the action of O3 gives VA. Reduction of 41.5
g. Et homocuminate with Na and EtOH gives 20.3 g. homocuminyl alc., b10
129° (p-xenylcarbamate, m. 144-5°); the bromide b14
136°; 30 g. with MeCNaCO2Et)2 gives 34 g. Et
homocuminylmethylmalonate, b13 200°; 38 g. ester, 160 cc. H2SO4 and
60 cc. H2O, heated on the water bath for 3 hrs., give 10 g.
2-methyl-7-isopropyl-1,2,3,4-tetral-1-one, b12 155-60°
(phenylsemicarbazone, m. 180-1°; 2,4-dinitrophenylhydrazone, deep
red, m. 177-8°); the action of MeMgI and dehydrogenation gives VII,
b9 190-51° (picrate, orange-yellow, m. 92-3.5°;
sym.-trinitrobenzene derivative, yellow, m. 108-10°).
Tetrahydroeremophilone and MeMgI, followed by dehydrogenation give
1,3-dimethyl-7-isopropylnaphthalene, whose picrate, orange-yellow, m.
113-14.5°, and sym-trinitrobenzene derivative bright yellow, m.
141-2°. o-Methylbenzyl iso-Pr ketone. b. 125-6°, d2525
0.9652, nD25 1.5070 (40% yield); semicarbazone, m. 128-9°;
phenylsemicarbazone, m. 183°; the action of MeCHBrCO2Et and Zn and
dehydration with KHSO4, followed by reduction with Pd, give Et
γ-o-tolyl-α-methyl-β-isopropylbutyrate, b13 165°;
the action of H2SO4, followed by EtOH-KOH gives
2,5-dimethyl-3-isopropyl-1,2,3,4-tetral-1-one, b22 185-90°

(phenylsemicarbazone, m. 222-3°); reduction with Na and EtOH and dehydrogenation gives 1,6-dimethyl-7-isopropylnaphthalene, b13 154-8° (picrate, orange-red, m. 124-6°; styphnate, orange-yellow, m. 141-2°). Et homocuminylmalonate, b13 198°; 7-isopropyl-1,2,3,4-tetral-1-one, b17 158-60° (2,4-dinitrophenylhydrazone, m. 223-4°); EtMgI, followed by dehydrogenation, yields 1-ethyl-7-isopropylnaphthalene, b9 135-45° (picrate, deep yellow, m. 65-7°; sym-trinitrobenzene derivative, yellow, m. 79-81°). The absorption spectra of I and eremophilone are given; that of I is very similar to that of mesityl oxide.

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AN 1933:4745 CAPLUS
DN 27:4745
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TI Constitution of eremophilone and of two related hydroxy ketones from the wood oil of Eremophila Mitchelli
AU Bradfield, A. E.; Penfold, A. R.; Simonsen, J. L.
SO Journal of the Chemical Society (1932) 2744-59
CODEN: JCSOA9; ISSN: 0368-1769
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB During the investigation of the constituents of the oil from the wood of Eremophila Mitchelli, to be published elsewhere, were obtained eremophilone, C15H22O (I), m. 41-2°, 2-hydroxyeremophilone, C15H22O2 (II), m. 66-7°, and 2-hydroxy-1,2-dihydroeremophilone, C15H24O2 (III), m. 102-3°. I, b15 171°, m. 41-2°, d2525 0.9994, nD25 1.5182, [α]5461 -207° (MeOH, c 2.46); in CHCl3 I adds 2 mols. Br, after which HBr is evolved, leaving a viscid green oil; H2S passed into I in EtOH-NH3 with cooling gives a pale yellow addition product, which decomps. when separated; semicarbazone, decomps. 202-3°, [α]5461 -293° (MeOH, c 2.35). The presence of the group CH2COCH:CH is shown by the formation of a hydroxymethylene derivative, m. 105°, by the action of Na in Et2O and HCO2Am. Catalytic reduction of I gives tetrahydroeremophilone (IV), b17 165°, d2525 0.9641, nD25 1.4909, [α]5461 12.5° (MeOH, c 4.08); AmNO2 and HCl give a NO derivative, m. 139° (decomposition), and Na and HCO2Am give a liquid hydroxymethylene derivative; semicarbazone, decomps. 213-4°; oxime, m. 126-7.5°, [α]5461 17.2° (CHCl3, c 4.19); 2,4-dinitrophenylhydrazone, orange, m. 178-9°. Reduction of I with Na and EtOH gives dihydroeremophilol (V), b14 168-70°, nD25 1.5089, [α]5461 68.8° (MeOH, c 5.66); 3,5-dinitrobenzoate, m. 119-21°; oxidation gives IV. Dehydrogenation of II gives eudalene. Oxidation of V with O3 gives HCHO and 6-acetyl-4,9-dimethyl-2-decalol, analyzed as the 2,4-dinitrophenylhydrazone, orange, m. 146-9°; oxidation of the ketone with NaOBr gives CHBr3 and 4,9-dimethyl-2-decalol-6-carboxylic acid, m. about 155°. Oxidation of I with H2O2 gives the oxide, m. 63-4°, [α]5461 -208° (MeOH), c 1.94); catalytic reduction gives the dihydro derivative, m. 53-4°, [α]5461 -205° (MeOH, c 2.07). The oxide is not attacked by EtONa but with AcOH and AcONa there results II, identified as the Bz derivative II is a pale yellow, very viscid oil. b22 189-90°, m. 66-7°, d2525 1.0620, nD25 1.5564, [α]5461, 153° (MeOH, c 2.51); it oxidizes with extreme rapidity on exposure to the air; Bz derivative, m. 119-21°, [α]5461 162° (AcOEt, c 2.01); NH2OH gives a compound C15H23O2N, m. 157-8°. Oxidation of the Bz derivative with O3 gives Me2CO, a trace of HCHO and the anhydride (VI), m. 186-8°; the acid fraction contained BzOH and an oily acid, more conveniently prepared from VI with NaOH in MeOH; this acid, 9-methyl-Δ2-decalene-4,6-dione-2-carboxylic acid, was analyzed as the semicarbazone, m. 215-6° (in a bath preheated to 195°). Oxidation of II with H2O2 gave 3 compds.; 2-hydroxyeremophilone oxide, m. 150-1°, [α]5461 196° (MeOH, c 2) (Ac derivative, m.

122-3°); the other 2 products were the α- (VII) and β-forms of 1-methyl-4-(α-hydroxyisopropyl)cyclohexane-1-acetic-2-αa-lactic acid, m. 167-8° and decomps. 198°; the α-form with AcCl gives the A derivative of the lactonic acid, C17H26O6, m. 192-3°; the β-form gives an anhydride or a dilactone, m. 178°. Reduction and hydrolysis of the Bz derivative of II gives 2-hydroxytetrahydroeremophilone, analyzed as the oxime, m. 146°. III m. 102-3°, [α]5461 94° (MeOH, c 2.02); 2,4-dinitrophenylhydrasone, golden yellow, decomps. 239-41°; diacetate, m. 69-70°; 3.5-dinitrobenzoate, m. 145-6°. Catalytic reduction of III gives 2-hydroxytetrahydroeremophilone (VIII) (α-form), m. 84-5°, [α]5461 84.2° (MeOH, c 2.07) (oxime, m. 158-60°; 2,4-dinitropenylhydrazone, orange, m. 210-20°). Reduction of III with EtOH and Na gives a glycol, a viscid yellow oil; distillation with Se gives eudalene. Oxidation of III with O3 gives 6-acetyl-4,9-dimethyldecal-2-one-3-ol, whose semicarbazone m. 216-9° (decomposition); oxidation of III with H2O2 gives VII. Reduction of VIII with Na-Hg gives IV. Oxidation of VIII with H2O2 gives the acid C15H26O4, viscid oil; CrO3 gives 2-hydroxy-ω-dihydroeremophilone, analyzed as the 2,4-dinitrophenylhydrazone, pale S-yellow, m. 158-60°.